Carbon Aerogels from 5-methylresorcinol-formaldehyde gels

FERNANDO PÉREZ-CABALLERO

Süsinikaerogeelid 5-metüülresortsinoolist ja formaldehüüdist

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[...]
"mas, en llegando al paso
que es puerto en este mar de mi tormento,
tanta alegría siento,
que la vida se esfuerza y no le paso."
[...]

[...]
"But drawing near
That welcome haven in my sea of woe,
Such joy I know,
That life revives, and still I linger here."
[...]

(D. Quijote de la Mancha. II - LXVIII)

CONTENTS

ORIGINAL PUBLICATIONS

This thesis is based on the following publications, book chapters and patents, which are referred to by Roman numerals within the text:

I. Pérez-Caballero, F.; Peikolainen, A.-L.; Uibu, M.; Kuusik, R.; Volobujeva,O.; Koel, M. *Preparation of carbon aerogels from 5-methylresorcinol–formaldehyde gels*. Microporous and mesoporous materials 108 (2008) 230-236.

II. Pérez-Caballero, F.; Peikolainen, A-L.; and Koel, M. *Preparation of nanostructured carbon materials*. Proceedings of the Estonian Academy of Sciences 57 (2008) 1, 48–53.

III. Pérez-Caballero, F.; Peikolainen, A-L.; Koel, M.; Herbert, M.; Galindo A.; and Montilla, F.*Preparation of the Catalyst Support from the Oil-Shale Processing by-Product*. The Open Petroleum Engineering Journal, 1 (2008) 42- 46.

IV. *Peikolainen, A-L.; Pérez-Caballero, F.; and Koel, M. Low-density organic aerogels from oil shale by-product 5-methylresorcinol.* Oil Shale, 25 (2008), 3, pp. 348–358.

V. Patent EE200700032. 26.6.2007 (2007) from "Tallinn University of Technology". Authors: Peikolainen, A-L.; Pérez-Caballero, F. and Koel, M.

VI. Pérez-Caballero, F.; Peikolainen, A-L.; Uibu, M; Herbert, M.; Galindo, A.; Montilla, F.; Koel, M. *Oil Shale Phenolic Derived Aerogels as supports for Palladium Nanoparticles.* The Oil Shale Journal. Accepted.

VII. Book Chapter: Organic aerogels as resource for porous carbon material. Authors: Perez-Caballero, F.; Peikolainen, A-L.; Koel, M.; White, R.J.; and Clark, J.H. Accepted for a Langmuir 2009 upcoming publication.

ABBREVIATIONS

R   Resorcinol

MR   5-methylresorcinol

F   Formaldehyde

CA   Carbon Aerogel

$scCO_2$ Supercritical Carbon Dioxide

SCFs   SuperCritical Fluids

Tc   Critical Temperature

Pc   Critical Pressure

VOC   Volatile Organic Compounds

GRAS   Generally Regarded As Safe

SEM   Scanning Electron Microscope

TEM   Transmission Electron Microscope

BJH   Barret-Johner-Halendar

BET   Brunauer-Emmett-Teller

CSTR   Continuous Stirred Tank Reactor

HPLC   High Performance Liquid Chromatography

IL   Ionic Liquid

BSE   Back Scatter Detector

SILP   Supported Ionic Liquid Phase

Φ   Diameter of the gel

ΔΦ   Linear Shrinkage of the gel

INTRODUCTION

In Estonia, oil-shale is the most important local solid fossil fuel, being a major source of energy. By fuel and crude oil production a remarkable amount of by-products is generated. Oil-shale processing by-products such as phenolic mixtures have been used as raw material in the chemical industry only moderately (less than 8%). Alkylresorcinols have been used in pharmaceuticals, food additives, cosmetics, fungicides, dyes, high value photoactive resins and novolacs in the electronics industry, as additives in the plastic industry as well as UV protectors, antioxidants, and stabilizers in the rubber industry. This work will discuss yet another application of alkylresorcinols, i.e. the application of purified 5-methylresorcinol as a precursor to carbon aerogel preparation. The possible use of the carbon aerogel impregnated with both black palladium and Rhodium is proposed for catalytic purposes.

Carbon aerogel is a highly porous carbon material with low density and large specific surface area. These properties allow the usage of the gel as adsorbent, membrane and carrier of metal catalysts. Furthermore, carbon aerogels may be used as electrode materials because of their controllable porous structure and electrically conductive network.

The preparation of carbon aerogel starts with that of organic gel. The gel obtained is then dried under supercritical conditions. The dried gel is pyrolyzed in an inert atmosphere at high temperature and carbon aerogel are then obtained. The coexistence of micropores and mesopores can extend their potential for applications. Activation has been proven to be very effective to improve the porosity of carbon aerogels and increase their specific surface area. The activation time is crucial to selecting the final pore size and specific surface area. Studies on activation using H_2O instead of CO_2 have been reported.

Pekala was the first to prepare aerogels from organic materials in the 1980s, using resorcinol as a phenolic precursor. The most thoroughly studied method of aerogel preparation developed by Pekala employs resorcinol (R) and formaldehyde (F) as precursors, sodium carbonate as catalyst (C) and water (W) as solvent. The gel is prepared *via* a double-catalyzed base-acid synthesis, in the course of which it is first cured in basic conditions at 358 K for 36 h (preferably from 48 h to 7 days). The gel formed is then acid-washed at 318 K for 3 days to promote a further cross-linking of the internal network of the gel. This will impart stability to the gel structure, and remove the excess base. 5-methylresorcinol, due to its molecular structure is an attractive precursor, unlike resorcinol, as faster gelling could be expected. Also, another important aspect adds value- 5- methylresorcinol costs less.

The use of carbon as a catalyst carrier is widely recognized. To impregnate the carbon network with metal nanoparticles, several methods have been developed, most starting with the impregnation of an oxidized salt or metal complex followed by a metal reduction reaction. A number of methods for reduction of the metal have been employed including thermal decomposition in an inert atmosphere and chemical conversion with hydrogen or air. A relatively new method is the chemical reduction in supercritical fluids with a reducing agent such as hydrogen or an alcohol as well as thermal reduction in supercritical fluids.

AIMS OF THE STUDY

The main goal of the present work was related to the production of mesoporous materials obtained from Oil Shale by-product starting materials and their test in several application regarding catalysis. In order to achieve this goal, several steps were taken which can be summarized in:

- To develop a method for the production of carbon aerogels from 5-methylresorcinol (MR) leading to products characterized by relatively similar properties to those of carbon aerogels made from resorcinol;

- To evaluate the steps of the preparation of carbon aerogels and find the best conditions in which this compounds should be prepared in order to enhance their properties from the aquagel formed in its initial stage until the pyrolysis leading to a carbon aerogel;

- To determine the physical and chemical properties of the carbon aerogels obtained and to assess the differences between carbon aerogels made from MR and from R;

- To test their properties as carrier by impregnating their porous structure with specific metal complexes able to penetrate the carbon network and remained attached as reduced metals;

- To investigate their potential applications for making the process worthy to be taken into a industrial scale;

  - To develop a method for the impregnation of carbon aerogels with a Palladium complex in supercritical carbon dioxide bearing in mind the generally low solubility of metal complexes in this solvent;

  - To develop a method for the impregnation of carbon aerogels with a Rhodium complex in the supercritical carbon dioxide-ionic liquid mixture and test their activities in situ;

- To evaluate the possible advantages that MR-F carbon aerogels may have compared to R-F aerogels;

- To demonstrate the potentiality and interest in using the carbon aerogels prepared in this work as a possible alternative for resorcinol carbon aerogels.

1. LITERATURE SURVEY

Aerogels are highly porous substances with a very low density and large specific surface area. They have network structures with open branched mesopores. Such a structure affords an extremely low thermal conductivity and low sound velocity. The aerogels may be obtained as monoliths, granulates, films, or powders. Pekala *et al* [1,2] first reported the synthesis of organic hydrogels by the sol-gel polycondensation of resorcinol (1,3-dihydroxybenzene) and formaldehyde. They prepared resorcinol-formaldehyde (RF) aerogels which were then dried using supercritical carbon dioxide. These aerogels were pyrolyzed in an inert atmosphere at 1.323K, resulting in carbon aerogels [3]. The RF carbon aerogels have a high porosity (>80%) and large specific surface area (400-900 m^2g^{-1}). Finally, an activation at 1173K was carried out which increased considerably the specific surface area of carbon aerogels [4,5]. The latter have a great potential for being used as adsorbents, catalyst supports, electrode materials for capacitors and rechargeable batteries and materials for chromatographic separations [6,7,8].

1.1 Preparation of carbon aerogels

1.1.1 Starting materials and catalysts

The preparation of aerogels starts with the synthesis of aqueous colloidal solutions during which the chemical and physical structures of a polymer take shape. Formaldehyde is responsible for the cross-linking of aromatic molecules, the resorcinol/formaldehyde (R/F) molar ratio must be 0.4<R/F<0.7 [9]. Too high a quantity of the remaining formaldehyde induces the collapse of the mesoporous structure of gels, decreasing the pore volume of the aerogel synthesized. The lack of formaldehyde as a cross-linking reagent leads to a weak cross-linking between the aromatic molecules and thus, no proper gels are formed [10]. The amount of the catalyst used affects both the size of particles and transparency of gels. With increasing amount of the catalyst the size of particles decreases and the velocity of gelation increases [11].

The overall concentration of reagents in water is usually expressed by a molar ratio of water/resorcinol (W/R), which reflects the amount of the solid fraction in the gel. At a given catalyst concentration an increase of the amount of the solid fraction (R) leads to the formation of smaller pores and a faster gelation. For gel preparation either a basic or acid catalysis alone could be used, but the doubly catalyzed synthesis utilizing both of them is considered to be the most effective [12,13,14]]. The acidic conditions favor hydrolysis, making condensation a rate-determining step of gelation. Besides hydroxides, carbonates have also been used as basic catalysts [15,16]. The second step using an acid catalyst promotes polycondensation [17,18,19,20]. The typical gelation temperatures used in case of resorcinol gels were in the range of 50-90°C

[21].As the temperature increases, the rate of gelation increases as well. In the present study, gelation times have been decreased from the typical 2-4 days to 1-2 hours as one of the consequences of changing the reactive resorcinol for its derivate 5-methylresorcinol (MR). The physical properties of the gels produced are similar to those of RF gels as will be shown below in this work.

Principally, a gel is composed of two phases, viz. a liquid phase filling the pores, and a solid phase. In order to obtain porous materials, the liquid phase has to be removed without a significant shrinkage of the solid material [22]. Because of the absence of the surface tension in supercritical conditions, supercritical carbon dioxide (sc-CO_2) was used to extract the solvent phase and, consequently, to dry the gel. Using $scCO_2$ is rational as its critical point can be easily attained. However, before $scCO_2$ can be used, water in the liquid phase must be replaced with other CO_2-soluble solvents, e.g. acetone or methanol. For this reason, the gel was left in an acetone bath of a volume 4-5 times that of the gel for 4 days, renewing acetone every 24 hours prior to the drying. Both the shrinkage and density of the aerogels prepared from R-F, using a direct supercritical acetone drying, were found to be higher than those of the aerogels prepared by the $scCO_2$-drying [23].

1.1.2. Thermal treatment to obtain carbon aerogels

The next step in the preparation of the carbon aerogel is the high temperature pyrolysis of the organic aerogel (usually at 973 - 1.273K). Upon pyrolysis the porous structure of the organic precursor is basically retained. During the process, carbon aerogels undergo a mass loss; leading to a volumetric shrinkage and densification relative to their pre-carbonized counterparts [24,25]. The resulting porous material is mainly composed of carbon. The size of pores is tailorable, as are the density and specific surface area.
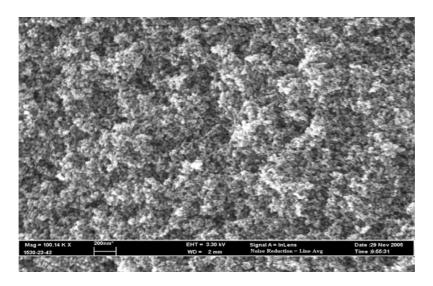

Figure I: SEM image of a typical carbon aerogel [II].

After the aerogel has been pyrolyzed into a carbon aerogel, activation is carried out at a temperature of 1173K for a number of hours in order to significantly increase the specific surface area of carbon materials [26,27].
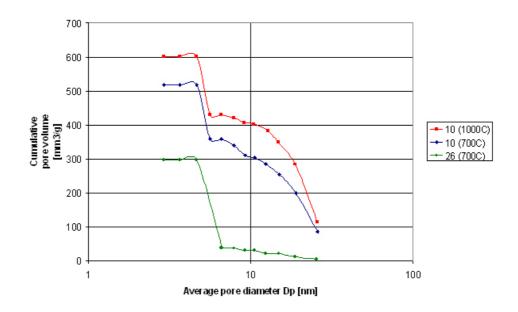

Figure II: The typical pore size distribution of two samples of carbon aerogel prepared from 5-MR at different pyrolysis temperatures [I].

1.2 Supercritical fluids

1.2.1. Introduction

Supercritical Fluids (SCFs) are substances which are simultaneously heated at above their critical temperature (Tc) and compressed above their critical pressure (Pc) [28].

In addition to their unique solubility properties, the SCFs possess certain other physicochemical properties that add to their attractiveness as solvents. Even though the substances possess the density, which is similar to that of liquids, they exhibit the diffusivity and viscosity similar to those of gases. Additionally, the zero surface tension of supercritical fluids allows a facile penetration of the latter into microporous materials.

At temperatures above Tc an isothermal compression results in a continuous increase in the fluid density, but no condensation to afford a liquid occurs. Supercritical fluids

fill the entire space available to them like gases, but, at the same time, can act as solvents for liquids or solids. The solvating properties may be tuned over a wide range by adjusting the fluid density. This can be achieved by changing either the temperature or pressure to some extent. This unique combination of tunable properties offers new approaches for the immobilization of organometallic catalysts and the solubilization of a wide number of compounds by modifying both the density and affinity of a supercritical fluid [29,30,31].
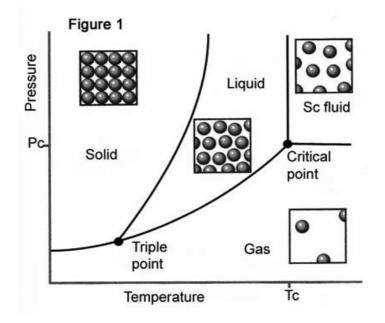

Figure III: A phase diagram in which the critical point is shown at the critical temperature (Tc) and critical pressure (Pc).

When a supercritical fluid is used as an extractive solvent, it is possible to separate a multicomponent mixture by capitalizing on both the differences in compound volatility and specific interactions between the mixture components and the SCF solvent. The application of SCF solvents is based on the experimental observation that many gases exhibit an enhanced solvating power when compressed to conditions above their critical point.

The motivation to develop the SCF solvent technology as a viable separation technique stems from:

1. a sharp increase in the cost of energy, which has increased that of traditional, energy-intensive separation techniques, such as distillation;

2. an increased governmental scrutiny and regulation of the use of common industrial solvents, such as chlorinated hydrocarbons, which has made nontoxic, environmentally friendly supercritical fluid solvents such as CO_2 very attractive as alternative industrial solvents;

3. a more stringent pollution control legislation, which has caused industry to consider

alternative means of waste treatment; and

4. increased demands on the performance of materials, which traditional processing techniques require high energy or the use of non-friendly chemicals.

It is of remarkable importance that the solvent power of a supercritical fluid can be related to the solvent density in the critical region. Thus, when operating in the critical region both pressure and temperature can be used to regulate the density and, therefore, the solvent power of the supercritical fluid. SCFs display a wide spectrum of solvent characteristics.

Carbon dioxide is by far the most widely used supercritical fluid (scCO$_2$), is non-toxic and non-flammable and can be handled safely on laboratory and industrial scales. Unlike classical organic solvents, CO$_2$ is not a volatile organic chemical (VOC) and its applications have a GRAS status (Generally Regarded As Safe). The economic viability of the scCO$_2$ technology has been demonstrated by commercial applications in natural product extraction [32], wood impregnation [33], wafer production and dry cleaning.

Examples of organometallic catalysis in supercritical fluids are by no means restricted to CO$_2$ [34], but to date only this medium has been used in applications focusing on catalyst immobilization. As many of the potential benefits of CO$_2$ for multiphase catalysis are also retained in the near-critical region, operation at or even below room temperature may be possible in many cases. In certain cases, low density CO$_2$ at temperatures above Tc can also be used for separation purposes, but generally densities over the critical point are required to exploit the solvent properties.

All methods of the immobilization of organometallic catalysts face paradoxical requirements for intimate contact of reagents with catalyst during the reaction, but a maximum of discrimination at the separation stage. Separation can be facilitated by introducing phase boundaries and confined spaces [35].

1.2.2. Extraction and drying of porous materials.

When a supercritical fluid is used as an extractive solvent, it is possible to separate a multicomponent mixture by capitalizing on both the differences in compound volatility and differences in the specific interactions between the mixture components and the SCF solvent. The applications of SCF solvents are based on the experimental observation that many gases exhibit an enhanced solvating power when compressed to conditions above their critical point. In order to dry the aerogels, they were placed in a sealed high pressure reactor and carbon dioxide was pumped in at 100 bars at room temperature. After two hours, the temperature was raised to 45ºC and CO$_2$ was pumped in a continuous extraction leading to the dried gel by elimination of the acetone existing in the pores. In figure IV, it can be seen how scCO$_2$ leads to a very homogeneous porosity whereas drying at room temperature and pressure leads to a gel characterized by a very heterogeneous surface and breaks all along its structure.
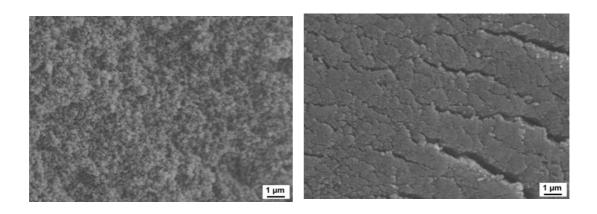
Figure IV: (Left) a SEM image of the gel dried using supercritical carbon dioxide. (Right) a SEM image of the gel dried at room temperature and pressure [III]

1.2.3. Activation of carbon aerogels

Activated carbon aerogels are obtained by the CO_2 activation of carbon aerogels. The increase in the specific surface area is noticeable: being normally around $600 m^2/g$, it reaches well over $2300\ m^2/g$ after the activation of a typical MR/F carbon aerogel. The activation is carried out at 1,173K in a continuous flow of CO_2 for 1-4 hours. However, even such a harsh activation produces no change in the basic network structure of the substance which contains both micropores and mesopores [36].

1.2.4. Impregnation of carbon aerogels

The supercritical carbon dioxide has been extensively studied as a green medium for chemical reactions and separations. The $ScCO_2$ can dissolve solutes like a liquid does and yet possesses a low viscosity, high diffusivity and zero surface tension like a gas does. These unique properties make the substance an attractive medium for the delivery of solutes to areas with complicated surfaces and poorly wettable substrates to attain a high uniformity and homogeneity of the materials deposited. The unreacted materials and by-products of $scCO_2$ processes can be easily removed from the system by flushing the system with a fluid. Thus, a green, rapid and direct procedure to decorate porous carbon materials with a catalytic palladium by a simple reduction of hydrogen was first reported by Wai *et al* [37].

The supercritical fluid incorporation is an effective, efficient and clean way for

synthesizing supported nanocomposites, including nanosized thin metals on a wide range of surfaces, and highly dispersed nanoparticles with controllable metal content and particle size in various polymer membranes and porous materials.

The metallic nanoparticles prepared by the supercritical fluid incorporation route are very attractive for their size dependent electrical, chemical and magnetic properties, especially for the deposition of metal alloy nanoparticles. The impregnation of pure metal nanoparticles might be slightly more complicated due to the difficulty in solubilising a metal complex, releasing an isolated oxidized metal for an eventually controlled reduction of the metal and subsequent elimination of all ligands and the solubilising groups employed.

The nature of the organometallic precursor employed in the SCF incorporation influences the final metal content, particle size and distribution. The precursor should have a reasonably high solubility in SCF in order to achieve appreciable rates of impregnation.

The precursor should also have a low thermal decomposition temperature so that the metal particles would not sinter. Although the incorporation of fluorinated compounds can improve solubility in $scCO_2$, most of the fluorinated organometallic precursors are volatile resulting in a weak interaction between the precursor and the substrates, which may lead to particle agglomeration and low metal loading [38].

Carbon aerogels can also be impregnated *in situ* at the polymerization step. Recently Macías-García *et al.* [39] reported a green method in the course of which the catalyst was substituted by $ZnCl_2$ yielding mesoporous carbons decorated with Zn nanoparticles, which were subsequently pyrolyzed and activated.

The metal-doped carbon aerogels have been tested for catalysts. Köhler *et al.* tested the supported palladium for catalyst for the carbon-carbon bond construction (the Heck reaction) in organic synthesis [40]. Even though a considerable number of supports were tested, carbon showed interesting properties due mainly to its high specific surface area. In case of the latter the conversion of the reaction was considerably higher than with any kind of oxide and most zeolites tested. The influence of the support depends on the chemical nature of the compound and on the fact that the reproducibility of the influence of this support on the Heck reaction is satisfactory. Whereas the reaction selectivity is practically not influenced by the catalyst, the activity is controlled by the kind of support used. Based on this study an order was established according to the support effectiveness for the olefination of bromobenzene with styrene (conversion):

$$C > TiO_2 > ZrO_2 > MgO > ZnO > SiO_2$$

Moreover, the reduction temperature for silica and oxides is generally in the range of 250-600ºC whereas 70ºC is enough to reduce carbon-supported palladium quickly and effectively. In addition, the specific Pd surface area of CA was at least 3 times higher than that of any other support tested in the study.

Recently, the synthesis of supports with high catalyst content has become an important issue in almost every catalytic process. Danciu *et al.* showed that carbon aerogels can be used to produce Fe-, Co-, Ni-, Cu- and Pd-doped carbon aerogels with a much higher metal content than any substance reported previously [41]. The content of each metal was around 20%, with the exception of the Pd-doped carbon aerogel, whose metal content was as high as 46%. The Ni- and Pd- doped organic and carbon aerogels were studied as catalysts in the C-C coupling reactions [42]. It was demonstrated that the Pd-doped carbon can be reused several times in the successfully tested Mizoroki-Heck reaction.

The effect of solubility on the metal content in supported nanocomposites

The metal content of supported nanocomposites is determined by the amount of the precursor impregnated in the substrate (uptake) and the metal content of the precursor

Although it is possible to have high uptakes at low fluid phase concentrations, studies have indicated that with the same system, if the solubility of the precursor is low, the maximum metal content is lower than the content with a precursor with high solubility [43].

To understand the dynamics of solubility of a precursor in scCO$_2$, one should take into account that the latter has solvating properties which are similar to those of n-hexane [44],.The latter will also probably be dissolved in scCO$_2$ and *vice versa*. The exception is fluorinated compounds, whose solubility in scCO$_2$ is much higher than in alkanes. The incorporation of fluorinated groups to conventional ligands improved the solubility of the compounds in scCO$_2$. Its effect on solubility can be quite dramatic. For example, at 20.7 MPa and 40°C the solubility of Cu(hfacac)$_2$ in scCO$_2$ is 200 times higher than that of Cu(acac)$_2$ [45].

Particle formation mechanism and factors influencing the particle size and pore size distribution

In the literature, a large variety of average particle sizes for metal particles supported on a wide variety of surfaces by SCF incorporation have been reported.

Erkey *et al* [46] proposed that when the adsorbed precursors were decomposed by a thermal reduction in an inert atmosphere and at ambient pressure, the growth of particles is controlled by the surface diffusion of metal atoms and/or precursor molecules. During the *in situ* thermal reduction, when the temperature is increased, the adsorbed precursor molecules decompose in the scCO$_2$ phase and are then adsorbed on the sites vacated by the decomposed precursor molecules. These adsorbed molecules are in turn reduced and the process continues until all the

precursor molecules in the system are converted to the metal. When hydrogen is injected into the $scCO_2$-precursor solution, the reduction occurs at the surface of the platinum particles since the reaction is autocatalytic. The resulting particles at the surface continue to grow until the entire metal precursor or hydrogen in the CO_2 phase will have been consumed. The particle size achieved by the reduction of hydrogen in $scCO_2$ is larger than that obtained by the reduction of the precursor after depressurization. The Pt coating was formed on the surface of the carbon aerogel. This result has also been supported by Watkins *et al*. [47].

According to Watkins *et al*., the rate of formation and growth of particles are determined by that of the precursor reduction reactions. The dissociation of the H_2 surface involved in the incorporation is the rate-determining step. Because platinum and palladium can catalyze this process, the reduction can be initiated at lower temperatures, while for the other metals, which have no catalytic ability, the reaction can only take place at considerable rates at higher temperature. The rate of formation and growth of metal particles are determined by the type and amount of the precursor in the reaction.

In this work, palladium hexafluoroacetylacetonate [$Pd(C_4HF_6O)_2$], which is both soluble and easily reducible in supercritical carbon dioxide, was used to impregnate the porous carbon aerogels based on phenolic compounds from oil-shale processing water and thus, generating metallic nanoparticles. The latter are uniformly distributed on the surface of the carbon matrix, enabling it to be used as catalyst. The catalyst was successfully tested in the reduction of cis-cyclooctene.
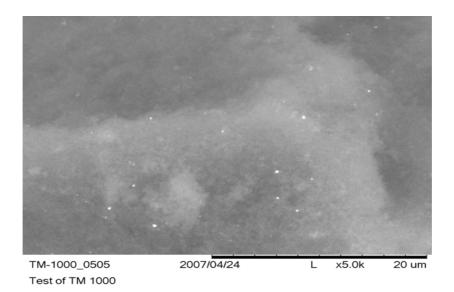

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Figure V: SEM picture of Pd particles deposited in the inner structure of a piece of carbon aerogel [VI]

Finally, carbon aerogels were used as carriers for the catalyzed reaction in a continuous flow for the hydroformylation of alkenes in Supercritical Fluid-Ionic Liquid Biphasic Systems in which a Rh complex was impregnated in the carbon aerogel by solving it in the ionic liquid layer [48].

1.3 Use of carbon aerogels for catalysis

The Palladium-doped carbon aerogels were first used for the reduction of cis-cyclooctene in the supercritical carbon dioxide. The reaction took place under mild conditions -just above the supercritical point of CO_2 - with a good yield, a good reuse of the catalyst and no leaching of Pd appreciated.

Secondly, the Rh doped in an activated carbon aerogel was the catalytic structure used for a continuous-flow hydroformylation of 1-octene in the binary supercritical fluid-ionic liquid biphase system. The catalyst leaching from the original reaction was minimized. Work is in progress to increase the yield of the reaction to render the latter economically and industrially interesting.

The main reasons why the hydroformylation of 1-octene was used were its mild conditions and green chemistry involved. It is a reaction which has a 100% Atom Economy (AE). Every year, its products are produced in millions of tons. Moreover, the chemoselectivity and regioselectivity of the reaction allow an easy separation and identification of the products. In the research, Rh was used in order to set it up as a new green alternative for the current commercialized Sasol process, which uses copper instead at 80 bars and 473K. Rh needs milder conditions. To develop a medium to stabilize Rh in a carrier is the main aim of the current research [49].

1.4 Nitrogen gas adsorption method

1.4.1 Total pore volume

Total pore volume, i.e. volume of the pores in a pre-determined pore size range can be determined from either the adsorption or the desorption phase. The volume pore size distribution is calculated according to the BJH model, the corrected Kelvin equation, assuming pores to be cylindrical (Barrett et all. 1951):

$$Ln\frac{P}{P_o} = \frac{-2\gamma V_L}{rRT}\cos\theta$$

This equation is used to calculate the relative pressure of nitrogen in equilibrium with a porous solid. In the equation, P is the value of the equilibrium vapor pressure of a liquid in a pore of radius r, Po is the equilibrium pressure of the same liquid on a plane surface, γ is the surface tension of the liquid, V_L is the molar volume of the liquid, Θ the contact angle with which the liquid meets the pore wall, R the gas constant and T absolute temperature.

1.4.2 The Specific surface area

Specific surface area is calculated according to the BET equation (Brunauer et al. 1938):

$$\frac{P}{V(P-P_o)} = \frac{1}{V_m c} + \frac{c-1}{V_m c}\frac{P}{P_o}$$

where *V* is the volume absorbed, V_m is the volume of monolayer, *P* is the sample pressure, P_o saturation pressure and *C* constant related to the enthalpy of adsorption (BET constant). The specific surface area (*S$_{BET}$*) is then calculated from *V$_m$* by the following expression:

$$S_{BET} = \frac{V_m n_a a_m}{mV_L}$$

where n_a is Avogadro constant, a_m the cross sectional area occupied by each nitrogen molecule (0,162 nm^2), m weight of the sample and V_L the molar volume of nitrogen gas (22414 cm^3). The theory is based on the assumption that the first adsorbed layer involves adsorbate/adsorbent energies, and the following layers the energies of the adsorbate/adsorbate interaction.

1.4.3 Advantages and limitations of nitrogen gas adsorption

Many parameters that describe the pore structure of a sample, like pore volume, specific surface area or pore size distribution can be determined with this method. One of the main drawbacks is that the time for analyzing one sample can be hours.

However, measurements can be made automatically for example during the night. The pore diameter can easily be determined from 0.3nm to 300nm, which is a range not covered by mercury porosimetry.

   Another limitation of nitrogen adsorption is that the cylindrical model is assumed in pore size distribution measurements, only open pores are determined. The desorption isotherm in the characterization of pore size distribution is affected by the pore network; when pressure is reduced, liquid will evaporate from large open pores, but pores of the same size that are connected to the surface with narrower channels remain unfilled. This changes the shape of the pore size distribution. Moreover, the samples come into contact with the temperature of liquid nitrogen (-196ºC) during analysis, which may destroy the sample [50].

2. EXPERIMENTAL

2.1 Synthesis of aquagels.

The anhydrous 5-methylresorcinol with a reported purity of 99.58% was obtained from Carboshale AS, Estonia. It was used as received. The anhydrous sodium carbonate with a purity of 99.8%, Riedel-de-Haen, Germany was used as received. The water used was purified using a Milli-Q Water system. The formaldehyde solution (37% w/w solution in water) was initially prepared from the paraformaldehyde powder (95% Aldrich). The formaldehyde solution (37% in water) was also obtained from Aldrich and was used as received. For the impregnation, the complex palladium hexafluoroacetylacetonate ($Pd(C_4HF_6O)_2$) was purchased from Sigma-Aldrich.

 5-methylresorcinol and formaldehyde aquagels were synthesized throughout a doubly-catalysed polycondensation process (figures VI). Sodium carbonate (C) was used as a base. The aquagels were obtained by curing the solutions at room temperature for 48 hours. The gelation times of the gels prepared were in the range of one to four hours, depending on the composition as will be shown below in this work. The molds used were test tubes characterized by an approximate diameter of 1 cm and a length of 10 cm, in which 80% of the total volume was occupied by the gel. After that, the gels were placed in an acetic acid solution (pH $\approx$ 4) and left there for another 48 hours, changing the acetic acid every 24 hours to favour hydrolysis as the rate-determining step of the gelation process. The MR-F aquagels prepared have the structure of a solid-like material filled with water. Being poorly soluble in CO_2, water was replaced by acetone over 4 days, renewing the latter every 24 hours [51].
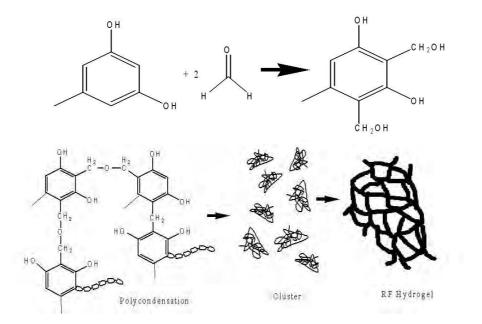

Figure VI: Possible mechanism for the polycondensation of methylresorcinol and formaldehyde to produce the aquagels.

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2.2. Supercritical CO_2 drying of gels

The drying of gels with CO_2 was performed in two steps. First, the gel was left in contact with a liquid CO_2 at a pressure of 12 MPa and room temperature. At those conditions the liquid CO_2 flowed through the reactor for two hours. After that, the temperature of the autoclave was increased above the critical temperature of CO_2 and acetone was extracted from the gel with the supercritical CO_2 at 318 K for six hours continuously. After the extraction, the extractor was slowly depressurized to atmospheric pressure and the MR-F aerogels were recovered. The supercritical drying process was performed using laboratory-made equipment which allows pressures of up to 30MPa and temperatures of up to 150ºC to be achieved.

2.3. Pyrolysis of aerogels

The pyrolysis of the dried aerogel was performed in an inert atmosphere (N_2) in a tubular furnace, at a working temperature of up to 1.373K, and controlled by a Nabertherm Program Controller S19 (Germany). The temperature program of the oven was continuously changed until an optimum was found. Generally the temperature was increased from room temperature at a rate of 10º/min until it reached 298K at which it was held for 25 minutes. After that, the temperature was increased again at a rate of 10º/min until 573K and held at that value for 60 minutes. Then, the temperature was increased to 550K and held at that level for 30 minutes. Finally the temperature reached the final pyrolysis temperature (from 973 to 1.273K). The gels were then left at the pyrolysis temperature for a number of hours. After pyrolysis, the furnace was cooled to room temperature under its own thermal mass.

The composition and morphology of carbon aerogels were analysed by an EDAX JEOL 6042 analyser and a Leo Supra 35 Scanning Electron Microscope (SEM). For nitrogen adsorption analyses, the Sorptometer KELVIN 1042 built by Costech International was used. The gas volume (N_2) adsorbed on the surface of materials at the temperature of a liquid nitrogen was measured. The precision of measurement was ≤3%. Helium was used as a carrier gas with nitrogen as an adsorptive gas. The BET specific surface area (S_{BET}) was calculated according to the Brunauer-Emmet-Teller (BET) theory. The specific micropore volume (Vmic) was determined via the t-plot and the pore size distributions were analyzed using the Barrett-Johner-Halendar (BJH) theory. To calculate the specific surface areas the P/Po range of 0.05–0.25 was used while to determine the micropore volumes the P/Po was from 0.0005 -0.4.

2.4. Activation of carbon aerogels

The activation of gels was carried out by placing carbon aerogels in a tubular furnace under the flow of an activating agent. The temperature was raised from room temperature to 1173K in two hours and then held at 1173K for a certain time. Finally, the oven was cooled down under its own thermal mass. H_2O and CO_2 were used as activating agents. The activation resulted in a relatively high increase in the specific surface area of gels, a notable decrease in their density and the modelling of their porous structure.

2.5. Impregnation and reaction set-up.

In order to impregnate carbon aerogels with palladium nanoparticles, a certain quantity of the gels was weighed and placed in a high-pressure reactor. Subsequently, $Pd(C_4HF_6O)_2$ was added together with a stirring bee. The reactor was then sealed and placed in a bath at 313K. The amount of the Pd complex weighed was in the range of 10-15 mass percent of the carbon aerogel mass. CO_2 was then pumped in up to a pressure of 15 MPa and the system was left for two hours in order to allow the palladium complex to dissolve. Then, a 15:1 mixture of CO_2:H_2 was pumped in until the final pressure in the reactor was 18.5 MPa. Then, the system was left to react for 25 minutes before a moderately slow decompression took place. After opening the reactor, the carbon decorated with palladium nanoparticles was obtained.

The resulting carbon-Pd catalyst was tested for performance in the reduction of cis-cyclooctene into cyclooctane in supercritical CO_2 having basically a total conversion in the quick reaction as will be described below. Moreover, an impregnated piece of carbon aerogel was reused several times in the same reaction reaching the same level of conversion without a loss in catalytic activity. The reaction was carried out in a cylindrical sealed 50mL reactor in which cis-cyclooctene and the impregnated carbon aerogel were placed. CO_2 was pumped in at 120 bars and 45ºC. Subsequently, the mixture of hydrogen and carbon dioxide was pumped in until reaching a final total pressure of 185 bars. Eventually, after 25 minutes of the reaction, the reactor was decompressed and the products were collected and directly evaluated by a UV-VIS Perkin-Elmer Lambda 25 UV/Vis Spectrometer.

2.6. Use of carbon aerogels as support of rhodium complex in the catalysis of the hydroformylation of terminal alkenes

ScCO$_2$, 1-octene, CO and H$_2$ were mixed and flown upwards through a tubular reactor (length 17.5 cm, internal diameter 5mm, external diameter 10mm) containing a catalyst composed of [PrMIM][Ph$_2$P(3-C$_6$H$_4$SO$_3$)](PrMIM=1-propyl-3-methylimidazolium), [Rh(acac)(CO$_2$)] (acacH=2,4-pentanedione) and [OctMIM][Tf$_2$N] (1-octyl-e-methylimidazolium bis(trifluoromethylsulfonamide)) supported on activated powered carbon aerogel. The effluent from the reactor was depressurised and the liquid products were collected for analysis by GC (organic products), NMR (ionic liquids) and ICPMS (Rh). A schematic diagram of the reactor is shown in Figure VII.
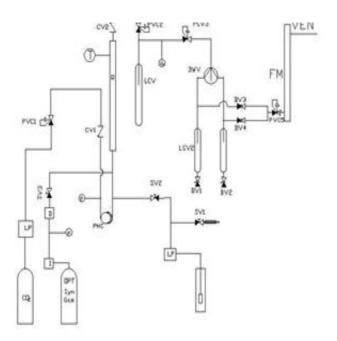

Figure VII: The hydroformylation of alkenes in a supercritical fluid-ionic liquid binary mixture.

The continuous-flow system is composed of a continuous stirred tank reactor (CSTR), a glass separator, a heat exchanger, two HPLC pumps, a pressure controller, two mass flow controllers for gases and a mass flow meter for liquids. The CSTR (100 cm^3) was fitted with an outside heating mantle, a thermocouple, a pressure gauge, a gas entrainment stirrer (1000 rpm), a gas/liquid inlet, an outlet port and a bursting disc. A separator was also fitted with a gas vent and a sampling port. The heat exchanger (S.S.) was a simple 1-1 tube-shell type. The pressure controller (Brooks Instrument) was used for down stream pressure regulation, keeping the pressure in the reactor constant independent of the variations in the inlet gas stream

pressure.

In Figure VIII the reaction catalysed by the Rh complex deposited in the ionic-liquid (IL) supported by the activated carbon aerogel is shown. For the design of the experiment, the stream of CO_2 transported both substrates and products through a fixed-bed reactor. The ionic ligands anchor the catalyst in the IL phase, which is not soluble in the SC phase. CO_2 is soluble in the IL phase and carries both gases and the substrate to the catalyst. No cross-contamination after decompression occurs [52].
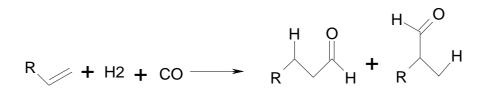

Figure VIII: Hydroformylation of terminal alkenes by reacting with syngas.

3. RESULTS AND DISCUSSION

3.1 Preparation of aerogels.

3.1.1 The chose of 5-methylresorcinol.

One of the main characteristics of the present work, is the use of the resorcinol derivative 5-methylresorcinol (MR) replacing resorcinol, that was undertaken for a number of reasons. Firstly, it was expected that the gels made from MR would have a stiffer structure to be reflected in a smaller shrinkage, possibly due to the presence of an additional directing methyl group. Secondly, MR as a by-product of the local oil shale-industry is readily available in Estonia and currently research leading to use 5-methylresorcinol is very well seen by the local authorities and Oil Shale industries, who funds a number of projects and believe its use would significantly reduce the pollution due to the unused by-product for generating energy or inserted directly into the chemical industry. Furthermore, after a few experiments, it was observed that the duration of gelation for gels made from MR was 10-20 times shorter than that of the gels produced from Resorcinol whereas other properties such as specific surface area and porosity remained unchanged (Table 1). Recently, an interest in shortening the time of synthesis of gels has noticeably increased [53]. Although no publications on the use of MR were available, the similarity between processes using resorcinol and phenol could be assumed.

When the aerogels were prepared from resorcinol (R) and formaldehyde, the shrinkage observed after drying in supercritical CO_2 compared to that for MR samples with the same molar ratios (MR/F = R/F = 0.5; MR/C = R/C = 60 and W/MR = W/R = 45) was more considerable when the extraction times were the same (almost 40%); that could possibly be due to an incomplete drying as the shrinkage for MR/F gels became slightly smaller when these were left for longer drying times than those used for drying MR/F samples[54].

The parameters of the drying process have been proven to be very important for the final appearance and properties of the aerogels resulting from the drying step. Moreover, this process is not highly time-consuming contrary to the whole process in general.

3.1.2 Optical properties of aquagels and aerogels.

As the gelation proceeds, the gel becomes more consistent and the backbone of the structure becomes stronger due to the interaction between the clusters produced by the polycondensation of 5-methylresorcinol and formaldehyde. During the polycondensation process, the color of the MR-F solution turned from colorless to yellow, orange and, finally to a reddish yellow. The transparency and intensiveness of the color of MR-F aquagels depended on the MR/C, MR/W or MR/F ratios used in the sol-gel polycondensation. Thus, as the W/MR ratio increases, gels become clearer being transparent at high catalyst concentration (MR/C < 50), gels did not gelate at high W/MR ratio when the amount of catalyst was insufficient (MR/C > 70). When both ratios are relatively small (W/MR < 35) and MR/C < 55) gels gelated quickly but the extraction with $scCO_2$ was not completed at the conditions specified above.

After the supercritical drying with CO_2 the MR-F aerogels were of the same color as MR-F aquagels but not transparent anymore; even though, as expected, the color turned to black after pyrolysis. In order to calculate the linear shrinkage of the gel, the following equation was used.

$$\Delta\Phi = \frac{\Phi_{before} - \Phi_{after}}{\Phi_{before}} x100$$

In Table 1 data on gelation time and shrinkage during the drying process are given. The gelation time, t, is the time needed to obtain a solid gel from the initial liquid mixture. This was controlled by tilting the vial by 45deg and observing the speed at which the fluid circulated by the walls being the time recorded when the solid does not circulate at all; and Φ is the diameter of the gel (cylinder shaped) before and after the supercritical extraction.

Since acetone interacts better with $scCO_2$ in terms of solubility, water was replaced by acetone before the extraction as described in the experimental section of this work.

The supercritical CO_2 drying was proven to be imperative in preserving the structure of the gels and in obtaining low densities and large specific surface areas. After extracting the gel with CO_2, the gel structure was very smooth and homogeneous with a well-distributed porosity and considerable specific surface. This was not achieved by drying by leaving the gel at ambient conditions.

Table 1. Characteristics of the aerogels prepared. All the gels were prepared with a ratio MR/F = 0.5. Φ refers to the diameter of the gel (cylinder shaped) before and after the Supercritical Extraction (SCE). $\Delta\Phi_{SCE}$ refers to the linear shrinkage of the gel described above.

Conditions	GEL color	Gelation time (min)	Φ before SCE (cm)	Φ after SCE (cm)	$\Delta\Phi_{SCE}$ (%)
MR/C = 31 W/MR = 43	Aerogel orange	150	1.060	0.855	19.33
MR/C = 60; W/MR = 62	Aerogel ligh brown	100	0.960	0.930	3.13
MR/C = 60; W/MR = 45	Aerogel yellow	140	0.975	0.950	2.5
MR/C = 31; W/MR = 24	Aerogel dark yellow	100	1.050	0.905	13.81
MR/C= 91; W/MR= 24	Aerogel pale yellow	60	1.070	0.910	14.95
MR/C= 92; W/MR= 43	Aerogel white-yellow	110	1.150	0.975	15.22
MR/C= 31; W/MR= 63	Aerogel Orange (transp.)	135	1.090	0.705	35.32
MR/C= 62; W/MR= 24	aerogel	100	1.115	0.890	20.18
MR/C= 95; W/MR= 62	Not gel at room Temperature				

The gel characterized by the following composition: MR/C=60; W/MR= 45 and F/MR=2, was obtained with an exceptionally low density (0.127 g/cm^3) and shrinkage. The densities and shrinkages of gels are highly affected by small changes in the temperature and the pressure during the extraction. A study on the influence of minimal changes of temperature and pressure the density and shrinkage of aerogels is a matter or further study.

3.2 Surface properties of carbon aerogels and activated carbon aerogels.

3.2.1 Surface properties of carbon aerogels.

The pyrolysis of gels in inert atmosphere at high temperatures leads to structures characterized by very high specific surface areas and tailorable pore size within the mesoporous/microporous range.

During pyrolysis, as it initially was carried out at 973K and 1273K, it was observed that at low carbonization temperatures, the V_{mic} and surface area were bigger than those pyrolyzed at higher temperatures due to the evolution of gases during carbonization (see table 2). This effect has been already identified as micropores that become less and less accessible to the probing gas nitrogen with increasing pyrolysis temperature. [55,56].

Table 2 shows the results of surface area and porosity measurements.

Gel Conditions	T_{Pyr} (K)	S_{BET} (m²/g)	$S_{non-mic}$ (m²/g)	S_{mic} (m²/g)	V_{mic} (mm³/g)	$\% S_{mic}$ .area (%)
MR/C= 31; W/MR= 43	973	442	61	381	134	86
	1273	241	146	34	95	40
MR/C= 60; W/MR= 62	973	462	43	420	148	91
	1273	383	220	163	57	43
MR/C= 60; W/MR= 45	1273	287	159	128	45	45
MR/C= 31; W/MR= 24	973	460	139	321	113	70
	1273	305	187	118	42	39
MR/C= 91; W/MR= 24	973	527	150	377	133	71
	1273	339	175	164	58	48
MR/C= 92; W/MR= 43	973	500	102	399	140	80
	1273	408	158	250	88	61

All the gels were prepared with a ratio MR/F = 0.5. $T_{Pyr.}$ refers to the temperature at which pyrolysis was carried out. $S_{BET}(m^2/g)$ is the BET surface of the carbon aerogel. $S_{non-mic} (m^2/g)$ is the surface of the non-microporous area of the carbon aerogel. $S_{mic} (m^2/g)$ is the microporous area of the carbon aerogel, $V_{mic} (mm^3/g)$ refers to the volume of the microporosity in the carbon aerogel, Φ is the diameter of the carbon aerogel and $\Delta\Phi_{pyr}$ is the linear shrinkage after pyrolysis.

The similarity between carbon aerogels and their precursors - organic aerogels in bulk density suggests that organic aerogels can be carbonized without a structural collapse.

At 1,273 K, the microporosity of the carbon aerogels studied is not as high as of those pyrolyzed at 973 K. Particle size depends on pyrolysis temperature. Thus, the BET surfaces were noticeable larger when pyrolysis was carried out at 973 K than when they were carbonized at 1,273 K. The observation in the decrease of the detected micropore volume when increasing the pyrolysis temperature has already been reported. It has been established to be due to a closing of the micropore entrances. [57,58]The optimization of the pyrolysis temperature in this range is a subject of further research.

Figure IX demonstrates the dependence of the size of pores on the surface of carbon aerogels on both composition and preparation conditions. In Figure IXb smaller particle sizes can be observed than in IXa. This may be explained by the better availability of the catalyst, which gives smaller particles as a result of the greater number of growing particles sticking together when forming the main network of the polymer. If the amount of the catalyst is smaller, the particles grow for a longer time. Consequently, nucleation affords larger pore sizes.
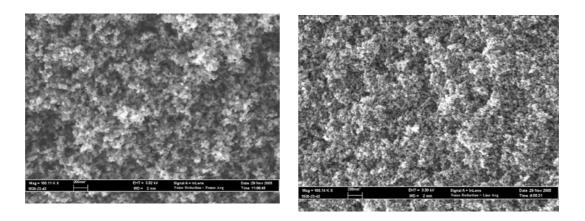

Figure IX: SEM images for gels prepared with low catalyst concentration(left) and high catalyst concentration(right).

Figure X shows the nitrogen adsorption isotherm of the gel prepared from MR/C= 91; W/MR= 24 and F/MR= 2, which was carbonized at 973 K, for a more quantitative comparison with the isotherms of Resorcinol-Formaldehyde carbon aerogels, some references can be consulted [59,60,61]. It can be seen that the isotherms are

characterized by the same amount of Nitrogen adsorbed at values of P/Po near zero. When P/Po approaches to 0,9 for R-F gels the slope becomes completely horizontal, meaning there is no increase in the volume of N_2 adsorbed when the pressure is increased. However, for MR-F gels, when the value of the pressure is of over 0.9, the slope is not horizontal at all, indeed it appears completely vertical, which reflects that it can still adsorb an important amount of gas since the saturation point for R-F gels appears over 0.1 units of P/Po earlier. [62]
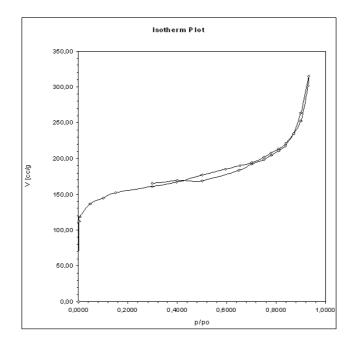

Figure X: A typical adsorption/desorption isotherm for a MR-F carbon aerogel.

Knowing the mass loss at different temperatures obtained from thermogravimetric analysis (see TGA curve on figure XI) it was possible to optimize the pyrolysis temperature program based on minimal evolution of degradation products resulted from slowing down the program rate for certain temperature intervals and taking into consideration of exothermic nature of reactions at temperatures around 570K. It appeared that there is no need for a final temperature as high as 1000ºC, and good results would be achieved by using the proposed temperature program because the change in mass was not noticeable at that high temperature.

The thermogravimetric studies showed that at temperatures of up to 300 °C, the rate of the mass loss of the gels was not as high as above 300 °C. It is for this reason that the heating rate of up to 10° per minute was used until reaching this temperature.

As reported in figure XII, the gel sample was then kept at 300 °C for one hour before raising the temperature because an exothermic reaction occurs at 300 °C. The temperature was then raised very slowly (2 °C/min) up to 550 °C as several reactions take place below 600 °C. Before raising it further, the temperature was again kept at 550 °C for 30 min and then raised at a rate of 10 °C per minute up to 780 °C.
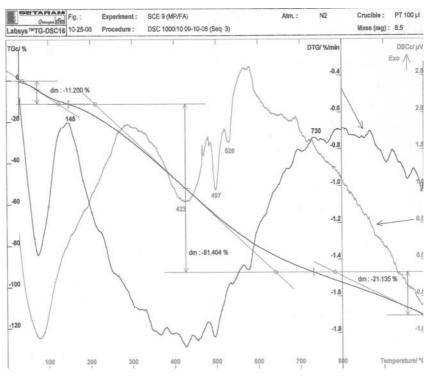

Figure XI: A Thermogravimetric diagram for a MR-F sample.

This temperature was taken as the final pyrolysis temperature because no intensive reactions occur above it. The choice of the final temperature depends on the requirements for pore size and specific surface area [63]. Above 780 °C, as the gel mass loss was very small, more time was needed to get a better activation of the gel, though no considerable changes were expected above the final temperature used in this study. There was a mass loss of the gels of over 80% at temperatures below 750 °C with most exo- and endothermic reactions observed taking place at temperatures between 400 and 650 °C. [II]·

The porosity of the gel can be characterized according to pore size. Macroporosity refers to pores greater than 50 nm in diameter; Mesoporosity, to pores greater than 2 nm and less than 50 nm in diameter. Microporosity refers to pores smaller than 2 nm.
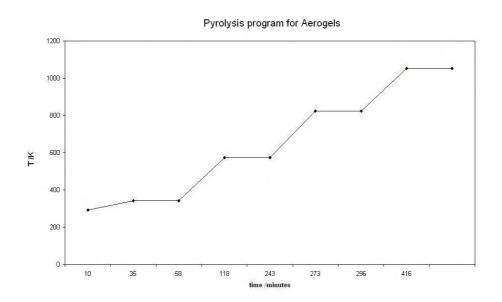
F*igure XII: Optimized temperature program for the pyrolysis of MR/F aerogels.*

The optimization of the pyrolysis program allowed the production of carbon aerogels characterized by a larger specific surface area and a higher microporosity. The study of the influence of the pyrolysis temperature and program on the final structure of carbon aerogels revealed the importance of this parameter in the monitoring of the final properties of carbon aerogels.

Table 3 shows the surface areas and pore volumes for gels pyrolyzed using common temperature programs and the program prepared after carrying out the thermogravimetric study, allowing their comparison. The Langmuir specific surface areas obtained using the new temperature program were higher than those obtained via the non optimized programs, particularly, in the case of the MR/C=60 gel more than two times greater. The porosity was also seen to be considerably enhanced as can be seen from the micropore and total pore volumes.

Table 3. Data on pyrolysis using optimized program at 1053K and other common temperature programs for some MR-F gels. na= not available

Pyrolysis ,	MR/C	W/MR	Langmuir Surface Area /m^2/g	Mic. V /mm^3/g	Total Pore Vol./mm^3/g
Optimised	60	45	790	120	640
Non Pyrolysed	60	45	390	0	441
Non-optimised	60	45	380	45	na
Optimised pyrolysis	90	45	700	160	360
Non Pyrolysed	90	45	170	0*	200
Non-optimised	90	45	640	140	na
Non-optimised	90	45	540	88	na

3.2.2 Surface properties of activated carbon aerogels (ACA).

CO_2 activation process is an effective way to introduce micropores in carbon aerogels, whose magnitude is enhanced paralelly with the increase in the activation time. CA has a network structure of primary carbon particles, providing predominant mesopores. These carbon particles have a few micropores relatively to their precursory organic aerogels, which have nearly no micropores. Activated carbon aerogels had a bimodal pore size distribution of micropores and mesopores. Activation treatment invites more micropores than carbonization process. Such an activation treatment does not change the basic network structure, so that Activated Carbon Aerogels have both abundant micropores and mesopores. It must be taken into account that weight loss during the activation is significant.

The properties of the samples activated by CO_2 and H_2O are shown in table 4. It can be seen how the activation by CO_2 greatly leads to an increase in the specific surface area whereas activating carbon aerogels with H_2O vapor poorly increases the specific surface area. It is interesting to observe that the percentage of microporosity is easily determined according to the activation time, thus, both for carbon dioxide and water, after two hours of activation with an increase in the amount of microporosity, its value starts to decay becoming almost half of the maximum value for CO_2 activation and losing over 15% for water activation.

Table 4. Data on activation of Carbon Aerogels using CO_2 and H_2O as activating agents. All samples were pyrolyzed at 1053K. The column "act agent" shows the gas flowed through the reactor during the activation process; t/h is the time of activation in hours. V. mic is the volume of micropores of the samples in mm^3/g. Total Pore V is the total pore Volume in mm^3/g. Mic Area and Non-Mic Area are the microporous and non-microporous areas respectively, in m^2/g. S_{BET} is the BET Specific Surface Area in m^2/g. % Mic is the percentage of microporosity in the sample.

Sample	Act. agent	t/h	V mic	Total pore V	Mic Area	Non- Mic Area	S_{BET}	% Mic	Density g/mL	Mass Loss (%)
Dried	--	--	0	nd	0	295,48	295,5	0	0,2061	--
Blank	--	0	82,92	nd	235,34	240,18	475,5	49,49	0,303	0
H_2O 1	H_2O	0,5	137,0	903,12	388,78	324,07	712,9	54,54	0,307	24,46
H_2O 2	H_2O	2	198,5	nd	563,21	207,39	770,6	73,09	0,311	25,09
H_2O 3	H_2O	4	149,4	876,25	423,96	257,93	681,9	62,172	0,287	42,99
CO_2 1	CO_2	0,5	263,2	812,91	746,96	281,32	1028,2	72,64	0,245	27,33
CO_2 2	CO_2	1	290,7	nd	825,11	144,30	969,4	85,11	0,217	33,40
CO_2 3	CO_2	1,5	472,4	nd	1340,9	248,92	1589,8	84,34	0,178	42,72
CO_2 4	CO_2	2	261,2	1253,3	741,1	914,63	1655,8	44,76	0,158	66,92

In figures XIIa and XIIb, the behavior of the activation is analyzed being CO_2 and H_2O the activating agents. Figure XIIa shows the percentage of microporosity of the samples which reaches over 85% for CO_2 activation and over 70% for H_2O activation. It is important to notice that he final porosity of the sample can be adjusted according to the activation time, thus, samples can be obtained with microporosity ranging from below 40% to over 80%. Figure XIIb shows the BET specific surface area of carbon aerogels after activation. After two hours of activation with CO_2, there seems to be reached a maximum as the value is not growing and the loss in the mass of the carbon aerogels does not allow measurements over the time studied. In the case of H_2O activation, no important changes in the specific surface area with the activation after a 4 hours study were observed.
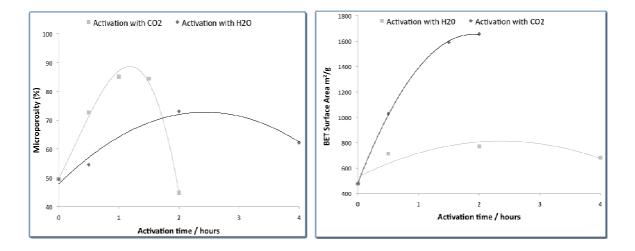
Figure XII. Microporosity (left) and BET surface area (right) are represented respectively vs Activation time for both H₂O vapor and CO₂ being the activating agents.

3.3 Applications of produced carbon aerogels

3.3.1 Impregnation of carbon aerogels with Pd nanoparticles.

 The next step was the impregnation of the carbon aerogel obtained. In regard to the impregnation, the use of $scCO_2$ as a carrier of the palladium complex into the pores is facilitated by the solvents lack of surface tension. The solubility of the metal complex in $scCO_2$ was crucial in order to allow metals enter the carbon network and deposit in the porous after reduction. Metal complexes are typically insoluble in $scCO_2$ but by employing the fluorous complex $[Pd(C_4HF_6O)_2]$, which showed sufficient solubility, this difficulty was overcome. Thus, the study of the deposition of many other metals through this process is now possible and interesting catalytic properties can now be studied and tested.   After a quick reduction with Hydrogen, Palladium remained deposited within the pores of the aerogel whereas the ligands remained dissolved and were taken off the reactor with the decompression.

  Figure XIII shows the composition of the core of the carbon aerogel after being impregnated with palladium nanoparticles. With the decompression in the reaction after reducing the Pd(II) complex, the particles of black Pd deposited all around the walls of the reactor as well as on the surface of the carbon aerogel. In order to carry out the analysis of the surface, the thin layer of black Pd formed was polished out.
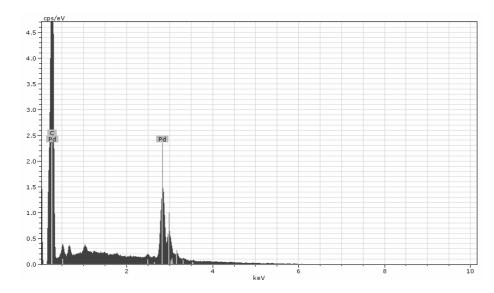
Figure XIII: Elemental analysis of palladium doped carbon aerogel.

The homogeneous distribution of black Pd (white dots) in the core of the carbon aerogel at two different scales can be observed in figure XIV. On the left, a sensitive to metal atoms Back Scatter Electron (BSE) detector is applied, and one can see how the particles of Pd occupy the inner of the carbon aerogel homogeneously. On the same figure, at the right side the same image is shown with no BSE detector applied. A homogeneous distribution of the catalyst in the carrier is a key fact in catalysis.

Figure XIV. SEM image of the composition of the carbon aerogel after impregnation with Palladium. Using BSE (left) and without that detector (right).

In this research, it was also found that after the impregnation process, the specific surface area, as well as the pore volume, decreased; meaning the pores were indeed being occupied.

In table 5 two gels with different composition are compared before and after impregnation with palladium: for the gel of composition MR/C = 60, a diminution in the Langmuir specific surface area of over 15% and in the micropore volume of over 40% was observed, indicative of the size of the palladium particles that remained within the network. However, for the gel of composition MR/C=90, there were no significant changes in the total Langmuir specific surface area whilst micropore volume decreased almost 30% after Pd impregnation. A more detailed study on the effects of impregnation on the specific surface area is in progress.

Table 5. N_2-adsorption data for aerogels with differing amounts of catalyst. Aerogels impregnated (Imp) are compared to those non-impregnated (N.Imp.). MR/C refers to the molar ratio 5-methylresorcinol to catalyst and W/MR water to 5-methylresorcinol. "Pore Vol." is the total volume of pores and "Mic. Vol" is the volume of micropores.

MR/C	W/MR		Langmuir Surface Area (m^2/g)	Pore Vol. (mm^3/g)	Mic. Vol. (mm^3/g)
60	45	N.Imp.	790	640	120
60	45	Imp.	660	620	70
90	45	N.Imp.	696	360	160
90	45	Imp.	695	345	115

The palladium coated support potentially possesses interesting applications in heterogeneous catalysis, for example, in continuous flow palladium catalyzed redox reactions employing a supercritical mobile phase, making the products of this work of interest for further study with a view to their industrial application in such processes. The method here demonstrated for support impregnation with palladium is also potentially adaptable for a range of other metal catalysts, facilitating production of supported catalysts for a variety of catalytic transformations.

The resulting carbon aerogel with palladium nanoparticles was used for hydrogenation of cis-cyclooctene. The first brief results demonstrated that this catalyst worked well with high yield during several cycles, but more detailed study of this is needed for full description of this particular kind of catalysts.

3.3.2 Continuous Hydroformylation over SLIP (Supported Ionic Liquid Phase).

 Another interesting application was studied in collaboration with the University of Scotland in which the hydroformylation of 1-octene (figure XV) catalyzed by Rh was carried out for comparison with the current process in which silica is used with small rhodium leaching.

Figure XV: products of the hydroformylation of 1-octene

 The hydroformylation was performed using both activated carbon aerogels and non-activated carbon aerogels. As it can be seen in table 6, the BET surface area is greater than that of silica in both kinds of carbon aerogel used. However the pore size distribution is drastically different being carbon aerogels characterized at the top limit of mesoporosity whereas silica pore diameter is smaller than 10nm.

 The reaction was carried out by mixing $scCO_2$, 1-octene, CO and H_2 upwards through a tubular reactor containing a catalyst composed of $[PrMIM][Ph_2P(3-C_6H_4SO_3)]$ (PrMIM = 1-propyl-3-methylimidazolium), $[Rh(acac)(CO)_2]$ (acacH = 2,4-pentanedione) and $[OctMIM][Tf_2N]$ (1-octyl-3-methylimidazolium bis(trifluoromethylsulfonamide)) supported on carbon aerogel.

 Even though the reaction is still under study in this conditions, interesting results were found as the Rhodium leaching for silica samples was much higher than for carbon aerogels in which the products solution came out completely colorless meaning not an important amount of Rhodium was lost whereas for the reaction using Silica as support, a significant amount of Rhodium was lost at the first stage of the reaction. The conversion to aldehyde was not improved using carbon aerogels, in fact, a poisoning of the pores seemed to occurred since the reaction takes place for a few minutes slowing down to zero afterwards. It is believed that the pore size of carbon aerogels has much to do with the nonworking process but more work is currently being processed to understand the difference in both mechanisms.

Table 6. BET surface area y pore diameter of carriers at several points during the reaction of hydroformylation.

Sample	BET Surface Area /(m^2/g)	BJH Adsorption average Pore diameter /nm
Silica	368	9,58
Carbon aerogel (CA)	536	44,03
Activated CA (ACA)	963	36,98
CA + catalyst(C)	133	54,18
ACA + C	214	39,74
CA + C - After reaction at 100 bars -	155	49,85
CA + C - After reaction at 150 bars -	152	38,36
ACA + C - After reaction at 100 bars -	238	39,83

CONCLUSIONS

The organic aquagels were synthesized by the sol–gel polycondensation of the new raw materials 5-methylresorcinol and formaldehyde. The MR–F aerogels were prepared by the supercritical drying in CO_2. The optimal conditions for obtaining the gels characterized by low densities and mesoporous structures were found to correspond to the molar ratios MR/F = 0.5, MR/C = 60 and W/MR = 45.

The carbon aerogels were subsequently obtained by pyrolysis of the MR–F aerogels in inert N_2 atmosphere having a large well-developed specific surface area and adaptable content of micropores (over 90%). The supercritical CO_2 drying was proven to be imperative in preserving the structure of the gels and in obtaining low densities and large specific surfaces. After extraction with CO_2, the gel structure was very smooth and homogeneous with a well-distributed porosity and considerable specific surface. This was not achieved by drying by leaving the gel at ambient conditions.

The possibility of controlling the mesoporous structure of aerogels by varying the amount of reactants, diluent and basic catalyst used in the polycondensation, as well as by varying the pyrolysis temperature has been demonstrated.

By using a scanning electron microscope (SEM), the images of the surface were obtained; also the distribution of pores in the carbon material was measured by nitrogen adsorption. The influence of different drying methods on parameters of material obtained was shown.

For aerogel preparation, 5-methylresorcinol and its technical mixture Honeyol™ are very competitive precursors beside well-studied resorcinol allowing controlling the gel structure easily by the same techniques, resulting in very similar characteristics. The whole extraction process took place in less than 4 h, the density and shrinkage being as low as 0.16 g/cm^3 and 3%, respectively. According to literature data the preparation of RF organic aerogels takes about 8 h or longer and the shrinkage is more considerable. Moreover, gels did not need high temperature for the gelation process. The MR–F gels were solid after an hour.

Optimization of the pyrolysis program allowed the production of carbon aerogels characterized by a larger specific surface area and a higher microporosity. The study of the influence of the pyrolysis temperature and program on the final structure of carbon aerogels revealed the importance of this parameter in the monitoring of the final properties of carbon aerogels.

The final properties of gels could also be tailored during pyrolysis and activation as was shown in this study. Samples with high microporosity and large specific surface area as well as samples with a higher value of the specific surface area characterized by being constituted by mesopores mainly were produced. The activation time of over 2 h led to too high mass loss and consequently, a total burn-off of samples when the activating agent was CO_2. In case of using H_2O the mass loss was below 50% during 4 h.

Using a CO_2-soluble palladium salt, the impregnation of carbon aerogels was successfully carried out. The process was quick, simple and produced excellent results, with the metal evenly deposited across the surface and inside the pores. Palladium deposited inside the micro porous structure of the gels decreased, as expected, the pore size of the samples as well as the total microporosity.

Studies on the impregnation of a Rhodium catalyst in a biphasic supercritical Fluid-Ionic Liquid have already been started to be investigated. Low leaching levels of the catalyst were achieved and an improvement in the selectivity and yield of the reaction under study is the main aim of this trend.

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mare come mai lo avevo conosciuto prima e mi avete fatto sentire spiritualmente ricco. Non so cosa ci riserverà il futuro, però vorrei che questo ringraziamento rimanesse in saecula saeculorum. Grazie mille Dèdè, Caterina, Martina, Salvo e i miei nonni! Veramente, tutto quello che ci insegnano nella scuola sono bugie: non avrei mai pensato che fosse possibile avere anche 6 nonni nella propria vita! Sfortunatamente ho conosciuto solo cinque nonni, ma ho ancora una nonna che in salute è più buona del pane trapanese con le olive!

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Afortunadamente, hace casi tres años, conocí a la mujer más maravillosa del mundo, la cual tuve la fortuna de desposar en una ceremonia digna de cuentos de hadas y princesas. Las irregularidades y curvas que guiaban mi camino se fueron convirtiendo en rectas y llanuras gracias a su ayuda. Cuando dos fuertes carácteres se unen, además de mentalidad caliente y mediterránea, el concepto de idealidad cambia y la situación se vuelve impredecible. La Diosa Fortuna se encarga de girar su rueda y nosotros intentamos permanecer agarrados a ella con los dos brazos. Sin el apoyo de Chiara Almanza hace ya años que hubiera abandonado este proyecto y elegido un camino más simple. Vale.

ABSTRACT

The systematics of the preparation of low density carbon aerogels from 5-methylresorcinol–formaldehyde (MR/F) organic aerogels dried in CO_2 under supercritical conditions is reported. The synthesis of organic aerogels involves a doubly catalyzed process: at first, in basic medium using sodium carbonate as catalyst and second, in acidic medium provided by acetic acid. The aquagels were obtained at room temperature within an hour. The carbonization of an organic aerogel leading to a carbon aerogel was carried out at temperatures around 1000K in the flow of dry nitrogen.

Carbon aerogels with a density of 0.18 g/cm^3 and specific surfaces of over 700 m^2/g were obtained. The optimization of the ratio of the components was carried out in order to achieve minimum shrinkage of the organic aerogel after drying. Regarding to the pore size distribution, it was found that the porosity of the materials obtained could be easily tailored by changing the synthesis conditions.

Thus, the conditions for obtaining materials with a preferential micro- or mesoporous structure were determined. The low-density organic aerogels formed by the supercritical carbon dioxide drying of 5-methylresorcinol–formaldehyde gels are a good source material for the preparation of low-density carbon aerogels with a homogeneous structure. In this research, the supercritical drying process was optimized so that the resulting aerogels would not significantly shrink during the process. The density of the resulting 5-methylresorcinol–formaldehyde organic aerogel was as low as 0.16 g/cm^3 and shrinkages of below 3% were achieved.

Moreover, the pyrolysis of the organic aerogel was optimized in relation to the flow rate of the evolution of pyrolysis products during the process. The carbon material obtained had a uniform structure, consisting of sparsely packed particles with a narrow size distribution. The aerogels obtained were examined using scanning electron microscope and nitrogen adsorption–desorption analysis.

Activation of carbon aerogel with CO_2 and H_2O was performed: the porosity and the specific surface area of activated carbon aerogels were studied. Langmuir specific surface areas of well over 2000 m^2/g were achieved and microporosity of carbon aerogel samples was tunable ranging from below 50% until over 85%.

Impregnation with the complex $[Pd(C_4HF_6O)_2]$ was carried out in supercritical CO_2 using H_2 for a quick reduction of Pd(II) to Pd(0) in a batch reactor in collaboration with the University of Seville. Eventually, highly porous materials decorated with nanoparticles of black palladium was obtained having a homogeneous metal distribution and an important use in catalysis with depreciable leaching of the catalyst and a considerable turnover in the reduction of cis-cyclooctene.

Finally, carbon aerogels were impregnated with a Rhodium complex previously dissolved in an ionic liquid. Its low vapor pressure allowed to achieve this impregnation and to carry out a reaction of hydroformylation of terminal alkenes in a continuous reaction being supercritical CO_2 the solvent in this process.

KOKKUVÕTE

Käesolevas töös on vaatluse all süsteemipärane väikese tihedusega süsinikaerogeelide valmistamine. Lähtematerjalina on kasutatud orgaanilist aerogeeli, mis on saadud 5-metüülresortsinool-formaldehüüd (MR/F) geelist seda ülekriitilise CO_2-ga kuivatades. Orgaanilise aerogeeli sünteesis kasutatakse geeli valmistamiseks kaheastmelist katalüüsi: esimeses etapis kasutatakse katalüsaatorina naatriumkarbonaati ning keskkond on aluseline, seejärel muudetakse keskkond äädikhappega happeliseks. Geel moodustub toatemperatuuril ühe tunni jooksul. Orgaaniline aerogeel muudetakse süsinikaerogeeliks pürolüüsi teel, kus materjali kuumutatakse ahjus temperatuuridel 1000 K lähedal juhtides pidevalt ahjust läbi inertset lämmastiku voolu.

Saadud süsinikaerogeelide tiheduseks mõõdeti 0,18 g/cm^3 ning eripinna suurus ületas 700 m^2/g. Et kuivatamise käigus geeli läbimõõdu vähenemine oleks minimaalne, optimeeriti komponentide koguste vahelisi suhteid. Pooride suuruse jaotuse uurimisel selgus, et saadud materjalide poorsust on lihtne reguleerida muutes sünteesi tingimusi.

Seega, määrati kindlaks tingimused, mille korral saada etteantud mikro- või mesopoorsusega materjalid. 5-metüülresortsinool-formaldehüüd orgaanilised aerogeelid on homogeense struktuuriga süsinikaerogeelidele heaks lähtematerjaliks, mille saamisel on oluline ülekriitilise süsinikdioksiidiga kuivatamise protsess. Selle uurimuse käigus optimeeriti ülekriitilise kuivatamise tingimusi, et saadavad aerogeelid protsessi käigus võimalikult vähe kokku tõmbuksid. 5-metüülresortsinool-formaldehüüd orgaanilise aerogeeli madalaimaks tiheduseks saadi 0,16 g/cm^3 ning minimaalne läbimõõdu vähenemine kuivatamisel oli alla 3%.

Järgmises töö etapis optimeeriti pürolüüsi tingimusi lähtudes pürolüüsiproduktide eraldumise kiirusest orgaanilisest materjalist. Pürolüüsi tulemusena saadi ühtlase struktuuriga süsinikaerogeel, mis koosnes kitsa suuruse jaotusega ning struktuuris hõredalt paiknevatest osakestest. Saadud aerogeele uuriti skaneeriva elektronmikroskoobiga ja analüüsiti lämmastiku adsorptsioon-desorptsioon meetodiga.

Eripinna suurendamiseks aktiveeriti süsinikaerogeeli CO_2 ja H_2O-ga ja uuriti aktiveeritud süsinikaerogeelide poorsust ja eripinna suurust. Langmuiri isotermi järgi saadi eripinna suuruseks üle 2000 m^2/g. Mikropooride osakaal süsinikaerogeelis oli reguleeritav ning jäi vahemikku 39% kuni 91%.

Süsinikaerogeel immutati [Pd(C$_4$HF$_6$O)$_2$] kompleksiga ülekriitilise CO_2 keskkonnas ning Pd(II) kiireks taandamiseks Pd(0)-ks kasutati vesinikku. Protsess viidi läbi perioodilises reaktoris ning toimus koostööna Sevilla Ülikooliga. Saadi väga poorne materjal, milles olid homogeenselt jaotunud metallilise pallaadiumi nanosuurusjärgus osakesed. Sellise materjali tähtis kasutusvaldkond on keemilises katalüüsis. Kui katalüüsi efektiivsus võib väheneda metalli eraldumise tõttu maatriksist, siis süsinikaerogeeli maatriksis olnud pallaadium säilitas cis-tsüklookteeni taandamisreaktsioonis efektiivsuse peale korduvat kasutamist.

Töö viimases etapis kasutati süsinikaerogeeli immutamiseks roodiumi kompleksi, mis eelnevalt oli lahustatud ioonses vedelikus. Ioonse vedeliku madal aururõhk võimaldas immutamist ja terminaalsetele alkeenidele formüülrühma tekkimise reaktsiooni läbi viia pideva protsessina, kasutades solvendina ülekriitilist CO_2-te.

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ELSEVIER

Preparation of carbon aerogels from 5-methylresorcinol–formaldehyde gels

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Abstract

The systematics of the preparation of low density carbon aerogels from 5-methylresorcinol–formaldehyde (MR/F) organic aerogels dried in CO_2 under supercritical conditions is reported. The synthesis of organic aerogels involves a doubly catalysed process: at first, in basic medium using a sodium carbonate catalyst and second, in acidic medium. The aquagels were obtained at room temperature within an hour. The carbonization of the organic aerogel to get a carbon aerogel was carried out at 973 K and 1273 K in the flow of dry nitrogen. Carbon aerogels with a density of 0.13 g/cm^3 and specific surfaces of over 500 m^2/g were obtained. The optimization of the ratio of the components was carried out in order to achieve minimum shrinkage of the organic aerogel after drying. Regarding to the pore size distribution, it was found that the porosity of obtained the materials obtained could be easily tailored by changing the synthesis conditions. Thus, the conditions for obtaining materials with a preferential micro- or mesoporous structure were determined.
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Keywords: Supercritical drying; Nitrogen adsorption; Supercritical carbon dioxide; Organic aerogel; Carbon aerogel; Porosity

1. Introduction

Aerogels are highly porous materials with very low density and large specific surface area. Their structure represents a network with open, branched mesopores. Such structure affords interesting properties, such as extremely low thermal conductivity and low sound velocity. The aerogels can be obtained as monoliths, granulates, films, or powders. Pekala [1] and Pekala and Alviso [2] have reported the synthesis of organic hydrogels by the sol–gel polycondensation of resorcinol (1,3-dihydroxybenzene) and formaldehyde and have prepared resorcinol–formaldehyde (RF) aerogels which were then dried using supercritical carbon dioxide. These aerogels were pyrolyzed in inert atmosphere at 1323 K resulting in carbon aerogels [3]. The RF carbon aerogels have a high porosity (>80%) and large surface area (400–900 m^2/g). The carbon aerogels have a great potential for being used as adsorbents, catalyst supports, electrode materials for capacitors and rechargeable batteries and materials for chromatographic separations [4].

The process of preparation of aerogels starts with the synthesis of aqueous colloidal solutions during which the formation of the chemical and physical structures of a polymer takes place. Formaldehyde is responsible for the cross-linking of aromatic molecules, its molar ratio must be 0.4 < R/F < 0.7 [5]. Too high a quantity of the remaining formaldehyde induces the collapse of the mesoporous structure of gels, decreasing the pore volume of the aerogel synthesized on the one hand. The lack of formaldehyde as a cross-linking reagent leads to a weak cross-linking between the aromatic molecules and thus, no proper gels

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are formed [6]. The amount of the catalyst used affects the particle size and also the transparency of gels. Increasing the amount of the catalyst decreases the size of particles and accelerates the gelation [7,8].

The overall concentration of reagents in water is usually expressed by the molar ratio of water/resorcinol W/R, which reflects the amount of the solid fraction in the gel. At a given catalyst concentration an increase of the amount of the solid fraction (R) leads to the formation of smaller pores and a faster gelation. For gel preparation either a basic or acid catalysis alone could be used, but the doubly catalysed synthesis utilising both is considered to be the most effective [9]. The acidic conditions favour the hydrolysis, making the condensation a rate-determining step. Besides hydroxides, carbonates have also been used as basic catalysts [10,11]. The second step using an acid catalyst promotes polycondensation [1,2,12–15]. The typical gelation temperatures used in case of resorcinol gels were in the range of 50–90 °C [16]. The higher the temperature, the faster the gelation.

Principally, the gel is composed of two phases, viz. a liquid phase filling the pores, and a solid phase. In order to obtain porous materials, the liquid phase has to be removed without a significant change or shrinkage of the solid material [17]. Because of the absence of the surface tension in supercritical conditions, $scCO_2$ was used to extract the solvent phase and, consequently, dry the gel. Using $scCO_2$ is rational as its critical point can be easily attained. However, before $scCO_2$ can be used, water in the liquid phase must be replaced with other CO_2-soluble solvents, e.g., acetone or methanol. For this reason, the gel was left in an acetone bath of a volume 4–5 times that of the gel for 4 days renewing acetone every 24 h prior to the drying. Both the shrinkage and density of the aerogels prepared from R–F using a direct supercritical acetone drying were found to be higher than those of the aerogels prepared by the $scCO_2$-drying [5,18].

The next step in the preparation of the carbon aerogel is the high temperature pyrolysis of the organic aerogel (usually at 973–1273 K). Upon the pyrolysis the porous structure of the organic precursor is essentially preserved. During pyrolysis, the carbon aerogels undergo a mass loss;

leading to a volumetric shrinkage and densification relative to their pre-carbonized counterparts [19–21].

The current research of gel preparation using 5-methyl-resorcinol (MR) instead of resorcinol (R) was carried out for a number of reasons. First, it was expected that the gels made from MR have a stronger structure to be reflected in a smaller shrinkage, possibly due to the presence of an additional directing methyl group. Second, MR as a byproduct of the local oil shale-industry is readily available in Estonia. Furthermore, after a few experiments, it was observed that gelation the duration of gelation of the gels made from MR was 10–20 times shorter than that of the gels produced from R. Recently, an interest in shortening the time of synthesis of gels has noticeably increased [22]. Although no publications on the use of MR were available, the similarity between processes using resorcinol and phenol could be assumed. The aim of this study was to obtain materials of low density and minimum shrinkage and to find out optimum experimental conditions, as well as an optimum molar ratio of reagents.

2. Materials and methods

Anhydrous 5-methylresorcinol with a reported purity of 99.58% was obtained from CarboshaleAS, Estonia. It was used as received. Anhydrous sodium carbonate with a purity of 99.8%, Riedel-de-Haen, Germany was used as received. Water used was purified using a Milli-Q water system. Formaldehyde (37%, w/w solution in water) was prepared from paraformaldehyde powder (95% Aldrich).

5-Methylresorcinol and formaldehyde aquagels were synthesized using a doubly catalysed polycondensation. Sodium carbonate (C) was used as a base. The aquagels were obtained by curing the solutions at room temperature for 48 h. The gelation times of the gels prepared were in the range of 1–4 h depending on the composition as shown in Table 1, but the gel was always left for 48 h to enable the curing process to take place. The moulds used were test tubes characterized by an approximate diameter of 1 cm and a length of 10 cm, in which 80% of the total volume was occupied by the gel. After that, the gel was placed in an acetic acid solution (pH ≈ 4) and left there for another

Table 1
Characteristics of the aerogels prepared

Conditions	Gel	Gelation time (min)	Φ before SCE (cm)	Φ after SCE (cm)	$\Delta\Phi_{SCE}$ (%)
MR/C = 31; W/MR = 43	Aerogel	150	1.060	0.855	19.33
MR/C = 60; W/MR = 62	Aerogel	100	0.960	0.930	3.13
MR/C = 60; W/MR = 45	Aerogel	140	1.325	0.875	33.96
MR/C = 31; W/MR = 24	Aerogel	100	1.050	0.905	13.81
MR/C = 91; W/MR = 24	Aerogel	60	1.070	0.910	14.95
MR/C = 92; W/MR = 43	Aerogel	110	1.150	0.975	15.22
MR/C = 31; W/MR = 63	Aerogel	135	1.090	0.705	35.32
MR/C = 62; W/MR = 24	Aerogel	100	1.115	0.890	20.18
MR/C = 95; W/MR = 62	Not gel at room temperature				

All the gels were prepared with a ratio MR/F = 0.5. Φ refers to the diameter of the gel (cylinder shaped) before and after the supercritical extraction (SCE). $\Delta\Phi_{SCE}$ refers to the linear shrinkage of the gel.

48 h, changing the acetic acid every 24 h so that hydrolysis could be favoured as the rate-determining step of the gelation process. The MR–F aquagels prepared have structures filled with water. Being poorly soluble in CO_2, water was replaced by acetone over 4 days renewing the latter every 24 h [23].

Drying with CO_2 was performed in two steps. First, the gel was left in contact with CO_2 at a pressure of 12 MPa. The liquid CO_2 flowed through the reactor for 2 h. After that, the temperature of the autoclave was increased above the critical temperature of CO_2, and acetone was extracted from the gel with supercritical CO_2 at 318 K for 6 h. After the extraction, the extractor was slowly depressurized to atmospheric pressure and the MR–F aerogel was recovered. The supercritical drying was performed using laboratory-made equipment which allows pressures of upto 30 MPa and temperatures of upto 150 °C to be achieved.

The pyrolysis of the dried aerogel was performed at inert atmosphere (N_2) in a tubular furnace, with a working temperature of upto 1373 K, and controlled by a Nabertherm Program Controller S19 (Germany). The temperature program of the oven was as follows: the temperature was increased from room temperature at a rate of 10 K/min until it reached 523 K at which it was held for 80 min. After that, the temperature was increased again at a rate of 10 K/min until the pyrolysis temperature (973 or 1273 K) was reached. The gels were then left at the pyrolysis temperature for 4 h. After pyrolysis, the furnace was cooled to a room temperature under its own thermal mass.

The composition and morphology of the carbon aerogels were analysed by an EDAX JEOL 6042 analyser and a Leo Supra 35 scanning electron microscope (SEM). For nitrogen adsorption analyses, a Sorptometer KELVIN 1042 built by Costech International was used. The gas volume (N_2) adsorbed on the surface of materials at liquid nitrogen temperature was measured. The precision of the measurements data of the adsorbed gas volume was

$\leqslant 3\%$. Helium was used as a carrier gas with nitrogen as an adsorptive gas. The BET specific surface area (S_{BET}) was calculated according to the Brunauer–Emmet–Teller (BET) theory. The specific micropore volume (V_{mic}) was determined via the t-plot and the pore size distributions were analyzed using the Barrett–Johner–Halendar (BJH) theory. For the calculation of specific surface areas the range of P/P_0 was 0.05–0.25; for the determination of the micropore volumes P/P_0 was from 0.0005 to 0.4.

3. Results

As the gelation proceeds, the gel becomes more consistent and stiffer due to the interaction between the clusters produced by the polycondensation of 5-methylresorcinol and formaldehyde. During the polycondensation process, the colour of the MR–F solution turned from colourless to yellow, orange and finally, reddish yellow. The transparency and intensiveness of the colour of MR–F aquagels depend on the MR/C, MR/W or MR/F ratios used in the sol–gel polycondensation. After the supercritical drying with CO_2 the MR–F aerogels were of the same colour as MR–F aquagels. However, the colour turned to black after pyrolysis at temperatures above 773 K. In order to calculate the linear shrinkage, Eq. (1) was used.

In Table 1 data on gelation time and shrinkage during the drying process are given. The gelation time, t, is the time needed to obtain a gel. This was controlled by tilting the vial by 45°, and Φ_{SCE} is the diameter of the gel (cylinder shaped) before and after the supercritical extraction:

$$\Delta\Phi = \frac{\Phi_{before} - \Phi_{after}}{\Phi_{before}} \times 100. \quad (1)$$

All experiments on preparing MR–F gels were performed at room temperature, because gelation times were short enough. For comparison, the aerogels from phenol–formaldehyde and resorcinol–formaldehyde solutions were also

Table 2
Results of N_2-adsorption on some carbon aerogel and aerogel samples

Gel conditions	T_{Pyr} (K)	S_{BET} (m²/g)	$S_{non-mic}$ (m²/g)	S_{mic} (m²/g)	V_{mic} (mm³/g)	%S_{mic} area (%)	Φ (cm)	$\Delta\Phi_{pyr}$ (%)
MR/C = 31; W/MR = 43	973	442	61	381	134	86	0.615	28.07
	1273	241	146	34	95	40	0.550	35.67
MR/C = 60; W/MR = 62	973	462	43	420	148	91	0.675	27.42
	1273	383	220	163	57	43	0.675	27.42
MR/C = 60; W/MR = 45	1273	287	159	128	45	45	0.610	32.00
MR/C = 31; W/MR = 24	973	460	139	321	113	70	0.600	33.70
	1273	305	187	118	42	39	0.590	34.81
MR/C = 91; W/MR = 24	973	527	150	377	133	71	0.675	25.82
	1273	339	175	164	58	48	0.650	28.57
MR/C = 92; W/MR = 43	973	500	102	399	140	80	0.760	22.05
	1273	408	158	250	88	61	0.700	28.21

All the gels were prepared with a ratio MR/F = 0.5. T_{Pyr} refers to the temperature at which pyrolysis was carried out. S_{BET} (m²/g) is the BET surface of the carbon aerogel. $S_{non-mic}$ (m²/g) is the surface of the non-microporous area of the carbon aerogel. S_{mic} (m²/g) is the microporous area of the carbon aerogel and finally, V_{mic} (mm³/g) refers to the volume of the microporosity in the carbon aerogel and Φ is the diameter of the carbon aerogel. $\Delta\Phi_{pyr}$ is the linear shrinkage after pyrolysis.

prepared. When the aerogel was prepared from phenol, no proper gels were obtained within any reasonable time. In this case only a few drops of a solid material at the bottom of the tube were observed. The duration of gelation of R–F gels at the same conditions of preparation were 10–20 times longer than those of MR–F gels at room temperature. The addition of formaldehyde to 5-methylresorcinol takes place at positions 2, 4 and 6 of the aromatic ring due to the hydroxyl groups occupying positions 1 and 3 and methyl at position 5. This causes a relatively fast gelation in comparison to the gelation of resorcinol and formaldehyde which involved two directing groups.

When the aerogels were prepared from resorcinol (R) and formaldehyde, the shrinkage observed after drying in supercritical CO_2 for MR and R samples with the same molar ratios (MR/F = R/F = 0.5, MR/C = R/C = 60 and W/MR = W/R = 45) was more considerable in the resorcinol system if the extraction times were the same (almost 40%); that could possibly be due to an incomplete drying as the shrinkage for MR/F gels became slightly smaller when these were left for longer drying times than those used for drying MR/F samples [24].

Table 2 shows the results of surface area and porosity measurements.

In order to calculate the percentage of the microporous area, $\%S_{mic}$, the following equation was used:

$$\%S_{mic} = \frac{S_{mic}}{S_{BET}} \times 100\%. \tag{2}$$

4. Discussion

The parameters of the drying process have been proven to be very important for the final appearance and properties of the aerogels resulting from the drying step. Moreover, this process is not highly time-consuming contrary to the whole process in general. From Fig. 1, it can be seen that the surface of the gel is very homogeneous, being porous at the nanometric scale when dried under $scCO_2$ conditions (Fig. 1a). However, if the gel is left at room temperature, the surface appears to be full of breaks, the structure having collapsed and possessing no homogeneity whatsoever (Fig. 1b).

At low carbonization temperatures, the V_{mic} and surface area are enlarged due to the evolution of gases during carbonization. This effect has been already identified as micropores that become less and less accessible to the probing gas nitrogen with increasing pyrolysis temperature [25,26].

From Table 3, it can be clearly seen that the densities of MR/F and carbon aerogels do not differ much from those obtained of RF samples [27]. The gel characterized by the following composition: MR/C = 60, W/MR = 45 and F/MR = 2, was obtained with an exceptionally low density (0.127 g/cm³). The densities and shrinkages of gels are highly affected by small changes in the temperature and the pressure during the extraction. A study on the influence
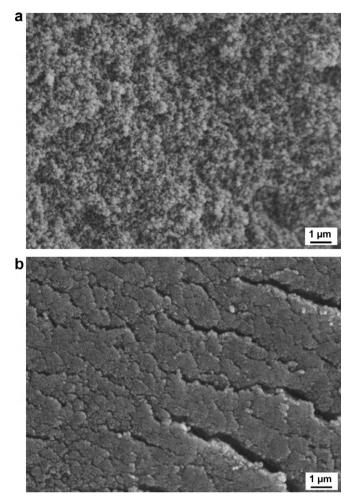
Fig. 1. (a) View of aerogel dried under supercritical conditions. (b) View of aerogel dried at ambient pressure and temperature.

Table 3
Data on the density of aerogels and carbon aerogels dried using $scCO_2$

MR/C	W/MR	Density SCE (g/cm³)	Density 973 K (g/cm³)	Density 1273 K (g/cm³)	$\Delta\Phi_{SCE}$ (%)
31	25	0.203	0.352	0.333	29.43
31	45	0.325	0.193	0.175	40.00
31	65	0.200	0.223	0.350	20.55
60	25	0.272	0.298	0.493	27.69
60	45	0.142	0.161	0.127	33.96
90	45	0.365	0.192	0.192	31.05

All the gels were prepared with a ratio MR/F = 0.5. Density SCE is the density of the aerogel after the extraction. Densities 973 and 1273 K are the densities of the carbon aerogels after being carbonized at 973 and 1273 K, respectively. Finally, $\Delta\Phi_{SCE}$ refers to the linear shrinkage of the gel after drying it.

of minimal changes of temperature and pressure the density and shrinkage of aerogels is a matter or further study.

The similarity between carbon aerogels and their precursors – organic aerogels in bulk density suggests that organic aerogels can be carbonized without a structural collapse. A comparison of the SEM images shows that the networks of organic and carbon aerogels obtained have a similar

morphology typical of aerogels prepared by supercritical techniques [28].

At 1273 K, the microporosity of the carbon aerogels studied is not as high as of those pyrolysed at 973 K. As seen from Fig. 2, particle size depends on pyrolysis temperature. Thus, the BET surfaces were noticeable larger when pyrolysis was carried out at 973 K than when they were
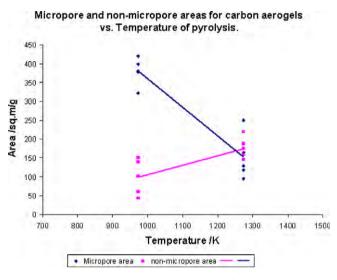
carbonized at 1273 K. The observation in the decrease of the detected micropore volume when increasing the pyrolysis temperature has already been reported. It has been established to be due to a closing of the micropore entrances [29,30]. The optimization of the pyrolysis temperature in this range is a subject of further research.

Fig. 3 demonstrates the dependence of the size of pores on the surface of carbon aerogels on both composition and preparation conditions. In Fig. 3b smaller particle sizes can be observed than in Fig. 3a. This may be explained by the better availability of the catalyst, which gives smaller particles as a result of the greater number of growing particles which stick together when forming the network. If the amount of the catalyst is smaller, the particles grow for a longer time. Consequently, nucleation affords larger pore sizes. Fig. 3c shows the surface of the carbon aerogel with the same characteristics than that in Fig. 3b, but which was carbonized at 973 K, whereas the pyrolysis described in Fig. 3b was carried out at 1273 K. It can be seen that the pore sizes of the gels given in Fig. 3c are smaller than those shown in Fig. 3b. Table 2 shows differences on pore size between aerogels carbonized at 973 K and at 1273 K, respectively. Fig. 4 describes the pore sizes of some of the samples whose composition and temperature of carbonization were changed.

Fig. 5 shows the nitrogen adsorption isotherm of the gel prepared from MR/C = 91, W/MR = 24 and F/MR = 2,

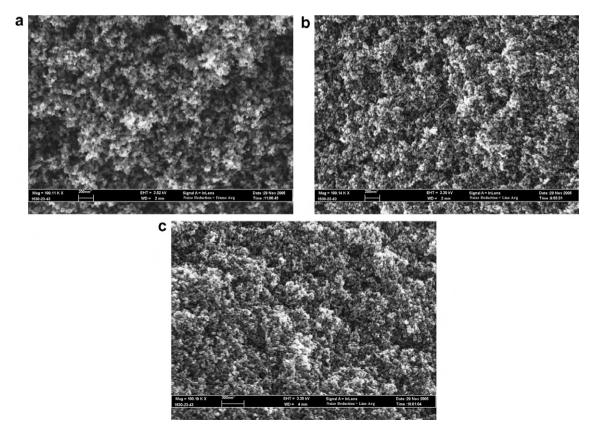Fig. 2. Microporous and non-microporous surface areas of carbons aerogels versus pyrolysis temperature.

Fig. 3. (a) MR/C = 92, W/MR = 44 and MR/F = 0.5, 1273 K pyrolysis. (b) MR/C = 30, W/MR = 24 and MR/F = 0.5, pyrolysed at 1273 K. (c) MR/C = 30, W/MR = 24 and MR/F = 0.5, pyrolysed at 973 K.
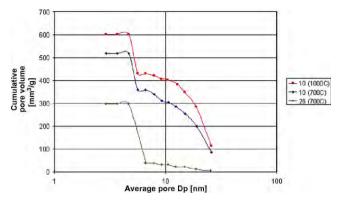
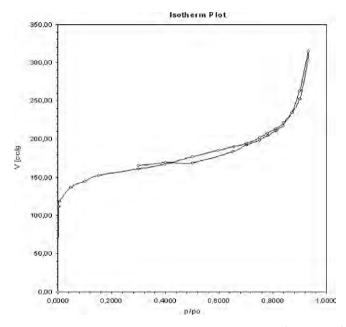Fig. 4. The BJH pore size distribution of some samples.

Fig. 5. The nitrogen adsorption isotherm of gel #12 (MR/F = 0.5, W/MR = 24 and MR/C = 90) pyrolysed at 973 K.

which was carbonized at 973 K, for a more quantitative comparison with the isotherms of resorcinol–formaldehyde carbon aerogels, some references can be consulted [31–33]. It can be seen that the isotherms are characterized by the same amount of ntrogen adsorbed at values of P/P_0 near zero. When P/P_0 approaches to 0.9 for R–F gels the slope becomes completely horizontal, meaning there is no increase in the volume of N_2 adsorbed when the pressure is increased. However, for MR–F gels, when the value of the pressure is of over 0.9, the slope is not horizontal at all, indeed it appears completely vertical, which reflects that it can still adsorb an important amount of gas since the saturation point for R–F gels appears over 0.1 units of P/P_0 earlier.

5. Conclusion

The organic aquagels were synthesized by the sol–gel polycondensation of the new raw materials 5-methylresor-cinol and formaldehyde. The MR–F aerogels were prepared by the supercritical drying in CO_2. The optimal conditions for obtaining the gels characterized by low densities and mesoporous structures were found to correspond to the molar ratios MR/F = 0.5, MR/C = 60 and W/MR = 45.

The carbon aerogels were subsequently obtained by pyrolysing the MR–F aerogels in inert N_2 atmosphere having a large well-developed specific surface area and adaptable content of micropores (over 90%).

The supercritical CO_2 drying was proven to be imperative in preserving the structure of the gels and in obtaining low densities and large specific surfaces. After extraction with CO_2, the gel structure was very smooth and homogeneous with a well-distributed porosity and considerable specific surface. This was not achieved by drying by leaving the gel at ambient conditions.

The possibility of controlling the mesoporous structure of aerogels by varying the amount of reactants, diluent and basic catalyst used in the polycondensation, as well as by varying the pyrolysis temperature has been demonstrated. By using scanning electron microscopy (SEM), the images of the surface were obtained, also the distribution of pores in the carbon material was measured by nitrogen adsorption. The influence of different drying methods on parameters of material obtained was shown.

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PUBLICATION II

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Preparation of nanostructured carbon materials

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Abstract. The low-density organic aerogels formed by the supercritical carbon dioxide drying of 5-methylresorcinol–formaldehyde gels are a good source material for the preparation of low-density carbon aerogels with a homogeneous structure. In our research the supercritical drying process was optimized so that the resulting aerogels would not significantly shrink during the process. The density of the resulting 5-methylresorcinol–formaldehyde organic aerogel was as low as 0.1 g/cm^3, its specific surface area being more than 350 m^2/g. Also, the pyrolysis of the organic aerogel to get carbon material with a proper structure was optimized in relation to the low rate of the evolution of pyrolysis products during the process. The carbon material obtained had a uniform structure, consisting of sparsely packed particles with a narrow size distribution. The density of carbon aerogels obtained was 0.2 g/cm^3, their specific surface area being over 700 m^2/g; the shrinkage was up to 30%. It was also found that the porosity of carbon aerogels could be varied by changing the conditions of synthesis. The aerogels obtained were examined using scanning electron microscopy, infrared spectroscopy, and nitrogen adsorption–desorption analysis.

Key words: materials science, carbon aerogel, supercritical drying, porous material.

INTRODUCTION

To prepare aerogels, which are highly porous materials with very low density and high specific surface area, in the first place a gel, which is composed of the solid and liquid phase independent of each other, is prepared. When the liquid phase is removed from the gel in a non-destructive manner, the solid porous material will be left with approximately the same shape and volume as the original gel. To avoid high capillary pressures within the pores from the surface tension caused by the receding liquid meniscus during the evaporation of liquids, in practice, supercritical extraction (SCE) is used for drying the gels [1].

Pekala et al. synthesized organic hydrogels by the sol–gel polycondensation of resorcinol (1,3-dihydroxy-benzene) with formaldehyde (F) and prepared resorcinol–formaldehyde (RF) aerogels by the supercritical drying with carbon dioxide [2]. In Estonia, 5-methylresorcinol (MR) as a by-product of the oil-shale industry is a cheap source material for this purpose. When using MR for the preparation of organic gels, the similarity to processes where resorcinol and phenol are used was assumed. To obtain gels with the lowest density and minimum shrinkage, the molar ratios of the reagents and experimental conditions have to be varied [3].

Aerogels can be obtained as monoliths, granulates, films, or powders. They can further be pyrolysed in an inert atmosphere at temperatures around 1000 °C to obtain carbon aerogels. The RF carbon aerogels have a high porosity (>80%) and large specific surface areas (400–900 m^2/g), which can be increased by the process of activation up to the values of over 2500 m^2/g [4]. The new direction in the field of carbon aerogels is the preparation of highly ordered mesoporous carbon materials [5]. Carbon aerogels can be used as adsorbents, materials for chromatographic separation, and electrodes for capacitors or fuel cells [6,7].

The preparation of aerogels starts with the synthesis of aqueous colloidal solutions where the chemical and physical structure of the polymer take shape. Formaldehyde is responsible for the formation of cross-linking aromatic molecules and should be used at a molar ratio of 0.4 < R/F < 0.7 since too much formaldehyde remaining induces a collapse of the mesoporous structure and

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decreases the pore volume of the aerogel prepared [8]. The amount of the catalyst in the solution affects the size of the particles formed as well as and the transparency of gels. Increasing the amount of the catalyst decreases the size of particles and pores and leads to a faster gelation [9].

A basic or acid catalyst can be used for the preparation of gels, but double-catalysed synthesis is considered to be the most effective [10,11]. Under basic conditions, formaldehyde is linked to an aromatic ring to form methylol (–CH$_2$OH) groups. The second step with an acid catalyst promotes polycondensation [12]. As for the basic catalysts, it has been shown that the valence and ionic radius of hydrated cations affect the orientation of the reaction path and the rate constant of the polymerization [13]. Besides hydroxides, also carbonates are used as basic catalysts [14].

The addition of formaldehyde takes place in the 2nd, 4th, and 6th positions due to the hydroxyl groups in the 1st and 3rd positions. As 5-methylresorcinol has in addition to two hydroxyl groups a methyl group in the 5th position, a relatively fast gelling in comparison with the resorcinol–formaldehyde gel formation could be expected.

In the case of resorcinol, the usual gelation temperature range used is 50–90 °C; the higher the temperature, the faster the gelling [2].

The amount of the solid fraction in the solution is expressed as the molar ratio of water/resorcinol, W/R. Increasing the amount of the solid fraction results in larger pores and a quicker gelling [11].

After the gel is formed and washed with acetic acid the solvent exchange step follows. The water within the pores of the gel is exchanged for the solvent miscible with CO$_2$ to carry out the SCE effectively.

In the preparation of carbon aerogel the next, last step is the pyrolysis of the organic aerogel. During pyrolysis the organic aerogels maintain the main carbon backbone of the structure. The carbonization affords a carbon aerogel with a highly porous structure, a large specific surface area, and a very low density. During pyrolysis, carbon aerogels also undergo mass loss, which leads to the volumetric shrinkage and densification relative to their pre-carbonized counterparts [15].

MATERIALS AND METHODS

In this study, 96% 5-methylresorcinol (a product of Carboshale, Estonia) was used as a phenolic precursor for organic gel. Formaldehyde (a 37% w/w solution in water) was prepared from paraformaldehyde powder (95%, obtained from Aldrich, Germany). Anhydrous sodium carbonate (99.8%, Riedel-de-Haen, Germany) and acetic acid solution (pH ~ 4) were used as catalysts,

and acetone (99.5%, Riedel-de-Haen, Germany) was used for solvent exchange.

5-Methylresorcinol and formaldehyde aquagels were synthesized using double-catalysed polycondensation. Sodium carbonate (C) was used as the base. The aquagels were obtained by curing the solutions at room temperature for 48 h. The gelation times of the gels prepared were in the range of one to four hours depending on the composition, but the gel was always left for 48 h to enable the curing process to take place. The moulds used were test tubes with an approximate diameter of 1 cm and a length of 10 cm, and the gel occupied 80% of the total volume of the tubes. After that the gel was placed in an acetic acid solution (10 times the volume of the gel piece) and left there for a further 48 h, changing the acetic acid solution every 24 h so that hydrolysis could be favoured as the rate-determining step of the gelation process. The MR–F aquagels prepared had pores filled with water. As it is poorly soluble in CO$_2$, the water was replaced by acetone after four days, renewing the latter every 24 h [16]; the amount of the acetone used for each exchange was 10 times the volume of the gel piece.

The drying with CO$_2$ was performed in three steps. First, the gel was introduced at a pressure of 20 MPa at 25 °C for 20 min to fill the pores of the gel with CO$_2$ and dissolve the acetone within. Then, the exit valve was opened and the extractor was depressurized to 12 MPa, letting the liquid CO$_2$ flow through the gel at 25 °C. The time for the liquid CO$_2$ flow through the gel was varied from one to two and a half hours. After this step the temperature was raised to 50 °C and CO$_2$ reached the supercritical state. The SCE lasted for two hours. After the extraction was completed, the extractor was slowly depressurized to atmospheric pressure and the MR–F aerogel was obtained.

The supercritical drying was performed using laboratory-made equipment that allows pressures of up to 30 MPa and temperatures of up to 150 °C to be achieved.

The pyrolysis of the dried aerogel was performed in a tubular furnace in an inert atmosphere (N$_2$) at a working temperature of up to 1100 °C, and controlled by a Nabertherm Program Controller S19 (Germany). The temperature program of the oven was as follows. The temperature was increased from room temperature at a rate of 10 °C/min until it reached 300 °C, at which it was kept for 80 min. After that, the temperature was increased again at a rate of 10 °C/min until the pyrolysis temperature (700 or 1000 °C) was reached. The gels were then left at the pyrolysis temperature for four hours. After pyrolysis, the furnace was left to cool down to room temperature.

The composition and morphology of the organic and carbon aerogels obtained were determined using an EDAX JEOL 6042 analyser, a Leo Supra 35 Scanning

Electron Microscope (SEM), and a Spectrum BX FT-IR System (Perkin Elmer), where IR measurements were obtained in the wavelength range from 4000 to 400 cm^{-1} using the KBr disk method. For nitrogen adsorption analyses, a Sorptometer KELVIN 1042 built by Costech International was used. The volume of the gas (N_2) adsorbed on the surface of the materials at a liquid nitrogen temperature was measured with an accuracy of over 97%. Helium was used as the carrier gas, nitrogen being the adsorptive gas. The Brunauer–Emmet–Teller (BET) theory was used to calculate the specific surface area (S_{BET}), the specific micropore volume (V_{mic}) was calculated according to the *t*-plot theory, and the pore size distribution, using the Barrett–Johner–Halendar (BJH) theory.

For thermogravimetric analysis SETARAM LabSys 2000 TG/DTA equipment was used. Experiments were performed in a N_2 (99.999%) flow of 100 mL/min at a heating rate of 10 °C/min in a Pt crucible. The sample mass was 8.5 mg.

RESULTS AND DISCUSSION

The formation of the gel starts in a colloidal solution where its chemical and physical structure take shape. The concentration of the reactants is given in molar ratios MR/F, MR/C, W/MR. The ratio W/MR describes the amount of the solid fraction in the gel.

In another study, a technical mixture containing 59.6% of 5-methylresorcinol (Honeyol™, a product of VKG, Estonia) was successfully used for the preparation of aerogels. The preparation process was based on the technology similar to the present one, and is described in detail elsewhere [17].

Supercritical drying of organic gels

The drying process has been proven to be very important for the final appearance and properties of aerogels. However, this process is the least time-consuming step among the other steps in the aerogel preparation: it took place in less than five hours whereas the whole synthesis needed a week to be fully completed. Because of its mild critical parameters (31.1 °C and 7.4 MPa), availability, and low price [18] CO_2 was used as a fluid.

Before and after the drying, the bulk gels were measured and their radial shrinkage and density were calculated. It was found that the lowest densities and shrinkages characteristic of MR–F aerogels were obtained when using molar ratios MR/F = 0.5, W/MR = 45, and MR/C = 60. At a ratio MR/C = 60 opaque gels with large pores were obtained. This enabled a short drying process and an almost complete removal of the solvent. Removal of the solvent can be assessed by measuring the shrinkage of the gel with the same composition after extended drying time. When the ratio MR/C = 16 was used, the pores of the gels were smaller and acetone was not extracted from the pores so easily. In this case, with a longer period of drying the shrinkage of the gels was less considerable and their density lower. The supercritical extraction four hours longer decreases the shrinkage by 11% and lowers the density more than 1.5 times. The relations between the catalyst amount, the drying time and the density and shrinkage of aerogels can be observed in Table 1.

The effect of the supercritical fluid drying on the porous structure of gels is illustrated in Fig. 1a and 1b.

Table 1. The effect of the catalyst amount and the drying time on the density and shrinkage of aerogels. MR/F = 0.5, W/MR = 45

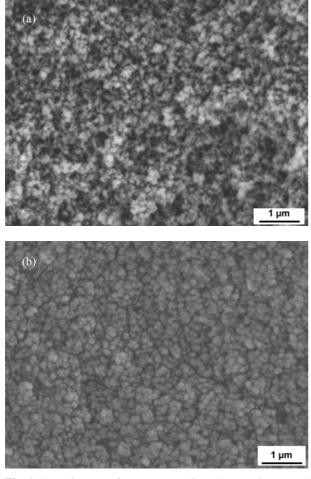| MR/C	CO_2 drying regime, h			Supercritical drying		Ambient drying	
	20 MPa, 25 °C	12 MPa, 25 °C	12 MPa, 50 °C	Density, g/cm³	Radial shrinkage, %	Density, g/cm³	Radial shrinkage, %
60	0.33	2.5	2	0.21	1	0.46	35
	0.33	2	2	0.21	2	0.46	28
	0.33	1.5	2	0.21	4	0.46	35
	0.33	1	2	0.21	3	0.46	33
16	0.33	2	6	0.58	27	1.35	45
	0.33	2.5	2	0.92	38	1.35	45

Fig. 1. SEM images of MR–F (MR/C = 60) organic aerogel dried by supercritical CO_2 extraction (a) and under ambient temperature and pressure (b).

With supercritical drying an aerogel with a sparse low-density structure was obtained. Drying at ambient temperature (25 °C) and pressure (1 atm) resulted in dense gel pieces that, due to capillary pressures, even cracked sometimes.

The MR–F gel formed in an acidic medium only was inhomogeneous and attracted no further attention, although its density and radial shrinkage were similar when dried either using SCE or under ambient conditions.

The aerogels were analysed using infrared spectrometry. In basic conditions the transmittance of IR is the lowest at 1000, 1500, and 1400 cm^{-1}. In these regions the IR radiation was absorbed by the substituted 5-methylresorcinol. Acetic acid dissolved part of this monomer turning the colour of the solution yellowish and making the gel more transparent for the IR radiation. The number of methylene (–CH$_2$– area 2930 cm^{-1} and 1450 cm^{-1}) and ether bridges (–CH$_2$–O–CH$_2$– area 1100 cm^{-1}) was almost equal in the gels prepared in basic and acidic media. The spectrum characterizing the

gels obtained by double-catalysed synthesis shows this type of catalysis not to be more advantageous than the one-step catalysis. However, after pyrolysis the aerogels prepared by double-catalysed base–acid synthesis shrank less and had lower density than those prepared using only the basic catalyst.

BET surface area measurements were carried out using the supercritically dried gels and an ambient dried aerogel. The specific surface area of the SCE dried aerogels is about 30 m^2/g larger than that of aerogels dried under ambient conditions.

Pyrolysis of aerogels

Carbon aerogels were prepared by the pyrolysis of organic aerogels in a tubular furnace. During the pyrolysis N$_2$ flowed through the reactor. The temperature program was adjusted after performing the thermogravimetry of organic aerogel samples (Fig. 2).

The thermogravimetric studies showed that at temperatures of up to 300 °C, the rate of the mass loss of the gels was not as high as above 300 °C. It is for this reason that the heating rate of up to 10 °C per minute was used until reaching this temperature. The gel sample was then kept at 300 °C for one hour before raising the temperature because an exothermic reaction occurs at 300 °C. The temperature was then raised very slowly (2 °C/min) up to 550 °C as several reactions take place below 600 °C. Before raising it further, the temperature was again kept at 550 °C for 30 min and then raised at a rate of 10 °C per minute up to 780 °C. This temperature was taken as the final pyrolysis temperature because no intensive reactions occur above it. The choice of the final temperature depends on the requirements for pore size and specific surface area [19]. Above 780 °C, as the gel mass loss was very small, more time was needed to get a better activation of the gel, though no considerable changes were expected above the final temperature used in this study. There was a mass loss of the gels of over 80% at temperatures below 750 °C and most exo- and endothermic reactions took place at temperatures between 400 and 650 °C.
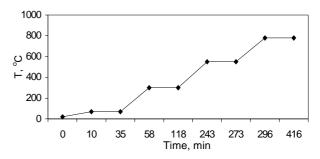

Fig. 2. An optimized pyrolysis program for converting aerogels into carbon aerogels.

The porosity of the gel can be characterized according to pore size. Macroporosity refers to pores greater than 50 nm in diameter and mesoporosity, to pores greater than 2 nm and less than 50 nm in diameter. Microporosity refers to pores smaller than 2 nm.

In this study, the technique used for the evaluation of the pore size distribution (PSD) allowed no study of microporosity. Figure 3, depicting the first derivative of the specific surface area with the pore diameter versus the pore diameter, shows a typical PSD of the carbon aerogel pyrolysed under the optimized temperature conditions and the final temperature of 780 °C as mentioned above. It can be seen that the gel is mainly microporous and mesoporous and only very little macroporosity is observed.

It is interesting to follow how the pore size distribution and BET surface area are affected by the temperature of pyrolysis. A conclusion can be drawn that microporosity decreases with increasing temperature of pyrolysis. Data on the porosity and specific surface area of carbon aerogels are presented in Table 2. It can be seen that in pyrolysed carbon aerogels micropores can be detected and the specific surface area is higher compared to the unpyrolysed aerogel. It must be mentioned that before the pyrolysis organic aerogels were mainly mesoporous, to a smaller extent macroporous, but not microporous whatsoever. It is interesting to note that pyrolysis carried out at an optimized temperature program (final temperature 780 °C) led to carbon aerogels with mainly a microporous structure and the highest specific surface area was obtained.

The size of the pores in the surface of carbon aerogels strongly depends on the composition of the organic gels and conditions of their preparation. The lowest density and specific surface area of the carbon aerogels obtained by our group were 0.2 g/cm^3 and 700 m^2/g, respectively. Although the facilities available did not allow more thorough analysis of porosity, it can be concluded that the gels prepared were microporous rather than mesoporous, which resulted in a considerably larger surface.
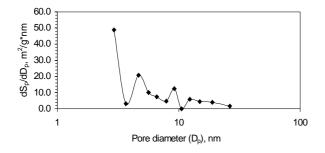

Fig. 3. A typical pore size distribution of the carbon aerogel pyrolysed at 780 °C.

Table 2. Pyrolysis of gel samples under different conditions. MR/F = 0.5, MR/C = 60, and W/MR = 45

Temperature/ pyrolysis program	BET surface area, m^2/g	$V_{micropores}$, mm^3/g	Non-micro-porous area, m^2/g	Micro-porosity, %
700 °C	450	130	55	88
1000 °C	290	47	160	45
Optimized at 780 °C	590	165	23	96
Unpyrolysed	140	Not detected	140	0

CONCLUSIONS

5-Methylresorcinol is an appropriate source compound for preparing organic aerogels by base or double-catalysed synthesis. Gels with the minimum shrinkage and density were obtained using molar ratios MR/F = 0.5, MR/C = 60, and W/MR = 45. The whole extraction process took place in less than 3.5 h, the density and shrinkage being 0.2 g/cm^3 and 3%, respectively. According to literature data the preparation of RF organic aerogels takes about 8 h or longer and the shrinkage is more considerable. It was also rather easy to manipulate the pore and particle size of the gel. Moreover, gels did not need high temperature for the gelation process. The MR–F gels were solid after an hour.

Optimization of the pyrolysis program allowed the production of carbon aerogels characterized by a larger specific surface area and a higher microporosity. The study of the influence of the pyrolysis temperature and program on the final structure of carbon aerogels revealed the importance of this parameter in the monitoring of the final properties of carbon aerogels.

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Nanostruktuurse süsinikaerogeeli valmistamine

Fernando Pérez-Caballero, Anna-Liisa Peikolainen ja Mihkel Koel

Väikese tihedusega süsinikaerogeelide valmistamisel on suurepäraseks lähteaineks väikese tihedusega orgaanilised aerogeelid. Artiklis on kirjeldatud 5-metüülresortsinool-formaldehüüdgeelist aerogeeli saamise metoodikat, mis seisneb geeli kuivatamises ülekriitilise süsinikdioksiidiga ja võimaldab vältida geeli poorsust tugevalt kahandavaid kapillaarjõude, ning süsinikaerogeeli saamise metoodikat, mille kohaselt orgaaniline aerogeel pürolüüsitakse inertses lämmastiku keskkonnas. On uuritud geeli koostist ja struktuuri ning mõõtmete vähenemist süsinikaerogeeli saamise erinevatel etappidel; on mõõdetud tihedust, pooride keskmist läbimõõtu ja eripinna suurust.

PUBLICATION III

Pérez-Caballero, F.; Peikolainen, A-L.; Koel, M.; Herbert, M.; Galindo A.; and Montilla, F.*Preparation of the Catalyst Support from the Oil-Shale Processing by-Product*. The Open Petroleum Engineering Journal, 1 (2008) 42- 46.

Preparation of the Catalyst Support from the Oil-Shale Processing By-Product

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Abstract: 5-methylresorcinol and the technical mixture of oil-shale phenolic compounds were applied for carbon aerogel preparation. Gels, which were prepared *via* base catalyzed polymerization were dried under supercritical conditions and subsequent pyrolysis of obtained dry aerogels led to carbon aerogels. Activation of carbon aerogel with CO_2 and H_2O was performed and porosity and the specific surface area of activated carbon aerogels were studied. Langmuir specific surface areas of well over 2000 m^2/g were achieved and microporosity of carbon aerogel samples was tuneable ranging from below 50% until over 85%. Impregnation with the complex $[Pd(C_4HF_6O)_2]$ was carried out in supercritical CO_2 using H_2 for a quick reduction of Pd(II) to Pd(0). Eventually, highly porous material decorated with nanoparticles of black palladium was obtained having a homogeneous metal distribution.

INTRODUCTION

In Estonia, oil-shale is the most important local solid fossil fuel, being a major source of energy. By fuel and crude oil production a remarkable amount of by-products is generated. Oil-shale processing by-products such as phenolic mixtures have been used as raw material in the chemical industry only moderately (less than 8%) [1]. Alkylresorcinols have been used in pharmaceuticals, food additives, cosmetics, biocides, fungicides, dyes, high value photoactive resins and novolacs in the electronics industry, as additives in the plastic industry as well as UV protectors, antioxidants, and stabilizers in the rubber industry [2]. This article will discuss yet another application of alkylresorcinols, i.e. the application of purified 5-methylresorcinol as a precursor to carbon aerogel preparation. Furthermore, the technical mixture of phenols generated in the oil-shale industry, Honeyol™, may be employed in carbon aerogel preparation without prior purification. The possible use of the carbon aerogel impregnated with black palladium is proposed for catalytic purposes.

Carbon aerogel is a highly porous carbon material with low density and large specific surface area. These properties allow the usage of the gel as adsorbent, membrane and carrier of metal catalysts. Furthermore, carbon aerogels may be used as electrode materials because of their controllable porous structure and electrically conductive network [3].

The preparation of carbon aerogel starts with that of organic gel. The gel obtained is then dried under supercritical conditions. The dried gel is pyrolysed in an inert atmosphere at high temperature and carbon aerogel will be obtained. The coexistence of micropores and mesopores can extend their potential for applications [4, 5]. Activation has been proven to be very effective to improve the porosity of carbon aerogels and increase their specific surface area. The activation

time is crucial to selecting the final pore size and specific surface area. Studies on activation using H_2O instead of CO_2 have been reported [6].

The use of carbon as a catalyst carrier is widely recognized [7, 8]. To impregnate the carbon network with metal nanoparticles, several methods have been developed, most starting with the impregnation of an oxidized salt or metal complex followed by the reduction [9-11]. A number of methods for reduction of the metal have been employed including thermal decomposition in an inert atmosphere and chemical conversion with hydrogen or air. The relatively new method is the chemical reduction in the supercritical fluid with a reducing agent such as hydrogen or an alcohol or thermal reduction in the supercritical fluid [12].

Pekala was the first to prepare aerogels from organic materials in the 1980s, using resorcinol as a phenolic precursor [13]. In the latter capacity, phenol [14, 15] and phloroglucinol [16] have also been used. The most thoroughly studied method of aerogel preparation developed by Pekala employs resorcinol (R) and formaldehyde (F) as precursors, sodium carbonate as catalyst (C) and water (W) as solvent [17]. The gel is prepared *via* a double-catalyzed base-acid synthesis, in the course of which it is first cured in basic conditions at 358 K for 36 h (preferably from 48 h to 7 days). The gel formed is then acid-washed at 318 K for 3 days to promote a further cross-linking of the gel. This will impart stability to the gel structure, and remove the excess base [13].

5-methylresorcinol, due to its molecular structure is an attractive precursor, unlike resorcinol, as faster gelling could be expected. Also, another important aspect adds value- 5-methylresorcinol costs less.

MATERIALS AND METHODOLOGY

Anhydrous 5-methylresorcinol (MR) with a reported purity of 99.58% was obtained from Carboshale AS, Estonia, and was used as received. Anhydrous sodium carbonate with a purity of 99.8%, Riedel-de-Haen, Germany was also used

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as received. The water used was purified using a Milli-Q Water system. Formaldehyde (a 37% w/w solution in water), Sigma-Aldrich, was used as received. Palladium (II) hexa-fluoroacetylacetonate [Pd(C$_4$HF$_6$O)$_2$] was obtained from Aldrich and was used as received.

Honeyol™ (H), which is a product of Viru Keemia Grupp, Estonia, was obtained from the Institute of Oil-Shale at Tallinn University of Technology; potassium hydroxide was from Chemapol Lachema Brno, Czech Republic; formaldehyde was in the form of a 35% w/w solution in methanol. The solution was made by dissolving paraform in methanol. Paraform (purity 95%) was from Sigma Aldrich Laborchemikalien GmbH, Germany; methanol used was an HPLC reagent, Rathburn Chemicals Ltd., Scotland.

The thermostat for gelation: a TECHNE Dri-Block® DB 3A, Spain; supercritical drying was performed on a modular extraction system (the extractor volume 100 mL) constructed by an NWA Analytische Mesgerate GmbH, Germany. Carbon dioxide with purity 99.8% was from Eesti AGA.

The gels based on 5-methylresorcinol were prepared using Pekala's procedure: 5-methylresorcinol and Na$_2$CO$_3$ were dissolved in water and the formaldehyde solution was added. The gel was formed at 298 K and after 24 h of curing, the gel piece was transferred into acetone prior to drying, replacing acetone every 24 h with the fresh one. The exchange of the solvent was carried out at least 4 times; every time the volume of acetone was ten times the volume of the gel piece. The gel was dried using supercritical CO$_2$.

The Honeyol™-formaldehyde gels were prepared by dissolving Honeyol™ in methanol, adding a 6% KOH solution in methanol and a 35% formaldehyde solution in methanol. Gelation was carried out at 333 K. Then the gel was dried using supercritical CO$_2$.

The pyrolysis was studied using MR-F aerogels. The carbon aerogels obtained were further used for impregnating with catalyst. The pyrolysis of the dried aerogel was performed in an inert atmosphere (N$_2$) in a tubular furnace, with a working temperature of up to 1053 K, and controlled by a Nabertherm Program Controller S19 (Germany). The furnace was cooled to room temperature under its own thermal mass after the pyrolysis was completed.

Activation was carried out after pyrolysis by leaving the gel in the tubular furnace and raising the temperature up to 1173 K in the flow of CO$_2$. H$_2$O was also used as activating agent.

The composition and morphology of organic and carbon aerogels were analysed by an EDAX JEOL 6042 analyser and a Leo Supra 35 Scanning Electron Microscope (SEM). For nitrogen adsorption analyses, a Sorptometer KELVIN 1042 built by Costech International was used: the gas volume (N$_2$) adsorbed on the surface of materials at liquid nitrogen temperature was measured. The precision of the measurements data of the adsorbed gas volume was ≤3%. Helium was used as a carrier gas with nitrogen as an adsorptive gas. The Langmuir specific surface area was calculated according to the Brunauer-Emmet-Teller (BET) theory. The specific micropore volume (V$_{mic}$) was determined *via* the t-plot and the pore size distributions were determined using the Barrett-Johner-Halendar (BJH) theory. To calculate the specific surface areas, P/P$_o$ was in the range of 0.05- 0.25; to determine the micropore volumes, P/P$_o$ was from 0.0005-0.4.

RESULTS AND DISCUSSION

Aerogel preparation

Similarly to resorcinol, 5-methylresorcinol is a trifunctional molecule with reaction sites at the 2nd, 4th and 6th positions of the aromatic ring where the addition of a bifunctional formaldehyde results in the formation of hydroxymethyl (-CH$_2$OH) groups. In case of 5-methylresorcinol the gel formation was faster and the temperature lower because of the presence of an additional directing group (-CH$_3$) in the 5th position of the aromatic ring unlike resorcinol. The gel was formed at 298 K within 100 minutes and was ready for handling after 24 h. The gel was directly transferred into acetone, excluding the step of aging in acidic media. The infrared spectrometric analysis showed no advantage of double-catalyzed synthesis over single-step base-catalyzed synthesis in bond formation. Neither the radial shrinkage during drying nor the density decreased due to curing in acidic media.

During the drying, the volume of the aerogel decreases compared to the gel that contains the solvent, especially if ambient pressure and temperature are applied while drying. During the conventional drying, the receding meniscus in the interface of the liquid and the gaseous phase lead to capillary pressure which shrinks the pores or even leads to the cracking of the fragile solid skeleton of the gel. To avoid the formation of the meniscus and generation of capillary pressures while drying, in the reactor supercritical state of the fluid must be used. At its supercritical state water is extremely reactive and the decomposition of polymer may occur. Because of its low critical parameters (T$_c$=304.25 K; P$_c$=7.38 MPa) carbon dioxide is the most suitable fluid to be used for supercritical drying. Carbon dioxide is also non-flammable, non-toxic, environmentally friendly and inexpensive and leaves no residues in the treated medium [18]. Also, the polarity of CO$_2$ is suitable for removing most of the organic solvents used for the sol-gel preparation of organic polymers [19]. In order to use supercritical CO$_2$ drying, water in the gel pores is replaced with another solvent miscible with CO$_2$. In this work acetone was used.

Attempts to prepare the Honeyol™-formaldehyde gel (H-F) in a similar way as MR-F gel showed that in case of the former a stronger basic catalyst for cross-linking and also higher temperatures for gelling are needed. The formation of the H-F gel is hindered because Honeyol™ contains apart from 59.6% of 5-methylresorcinol dihydroxy benzenes with additional substitutions at the positions where the directing groups would affect formaldehyde to react. The gel remained intact when methanol, which is also miscible with CO$_2$, was used for the solvent replacement instead of acetone. Further on methanol was used as a solvent throughout the process similar to [20].

The aerogel is composed of interconnected nanometre sized particles. The pore and particle size of the material can easily be tailored by varying the concentrations of components (reagents, catalyst and solvent). The most efficient method for modifying pore characteristics is changing the

amount of the catalyst in the sol: the higher amount of the catalyst affects the density, specific surface area and mechanical properties of dried aerogels. The shrinkage is the most considerable in case of gels prepared using a high loading of catalyst [21].

The optimization of concentrations of H-F and MR-F organic aerogels was carried out with the aim to achieving the lowest density and minimal radial shrinkage after drying [22-24]. In the experiments carried out by the authors an optimal duration of supercritical CO_2 drying was less than 4.5 h, as after a longer processing no further decrease in aerogel density or radial shrinkage was observed. The specific surface area was also measured. At optimal molar ratios, the drying shorter than 4.5 h resulted in the MR-F aerogel with a radial shrinkage of 2%, density of 0.21 g/cm^3 and specific surface area of 350 m^2/g.

In both cases the optimal concentrations of reagents were the following: MR/F=H/F=0.5, MR/C=H/C=60 and water/MR=methanol/H=60 (C- moles of catalyst). At the same molar ratios of the H-F the shrinkage of the aerogel was 29%, specific surface area 302 m^2/g and the density 0.10 g/cm^3. From Honeyol™, it was possible to prepare an aerogel with a specific surface area of 469 m^2/g. The shrinkage of the H-F aerogel was 20-30% due to the water generated in the polycondensation reaction. In case of Honeyol™ the double-step base-acid catalysis could not be favoured because it is known that in the presence of an acid catalyst, the unreacted formaldehyde present in methanol leads to the formation of hemiformal [25], hindering a further cross-linking between the molecules, which results in more considerable shrinkage. Infrared spectra also showed no advantage of double-catalyzed synthesized gels over the single-step catalyzed ones in terms of gel formation.

Carbon Aerogel Preparation

The microporosity of carbon aerogels can be tailored by modifying the pyrolysis conditions. Through the N_2-adsorption isotherm, information on the accessible surface area and overall porosity is generally obtained. The porosity that is not accessible for N_2 at 77 K can be considered a surface area reservoir that can be made accessible *via* activation. The carbon burn-off is an indicator of the micropore volume and surface area obtained during activation. *Via* the

CO_2-activation of carbon aerogels the surface area can be increased from 500 to well over 2000 m^2/g with the carbon burn-off of only 50%. It has been reported that the increase in the micropore volume more than 1 cm^3/g observed during the N_2-adsorption is due to an opening of initially inaccessible micropores and the creation of new voids [26]. A highly accessible surface area of the material is needed for applications in supercapacitors and fuel cells. Indeed, a large micropore volume is a prerequisite.

The pyrolysis was performed by placing the gels in a tubular furnace in the flow of nitrogen following the program described in Fig. (**1**). The final temperature of pyrolysis was 1053 K. This was shown to be optimum after having observed that the mass loss of the aerogel above this temperature is very low and the change in the porosity as well as specific surface area is negligible.
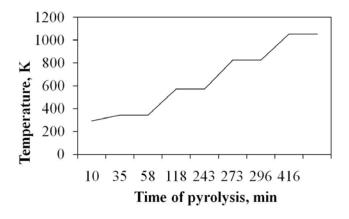

Fig. (1). The temprature program of pyrolysis.

Activation of Carbon Aerogel

Activation differs from pyrolysis in the temperature program and in the carrier gas. The effect of activation time on the porosity of the carbon aerogel was studied using H_2O or CO_2 as carriers in the reactor which was heated from room temperature up to 1173 K at a rate of 10 degrees per minute. After the final activation temperature was reached, the gel was left at this temperature for the time described in Table **1** as activation time. The table also presents the results of ni-

Table 1. Characteristics of the Samples Under Study

Sample	Activation Time, h	V_{mic}, mm^3/g	V_{total}, mm^3/g	S_{mic}, m^2/g	Langmuir Surface, m^2/g	%$_{mic}$	Density, g/cm^3	Mass Loss, %
Aerogel	—	0	NA$^+$	0	404.92	0	0.206	—
CA	0	82.92	NA$^+$	235.30	633.60	49.50	0.303	—
ACA-CO$_2$ 1	0.5	263.2	812.9	747.00	1429.17	72.60	0.245	27.33
ACA-CO$_2$ 2	1	290.7	NA$^+$	825.10	NA	85.10	0.217	33.40
ACA-CO$_2$ 3	1.5	472.5	NA$^+$	1341.00	2090.99	84.30	0.178	42.72
ACA-CO$_2$ 4	2	261.2	1253.3	741.20	2289.99	44.80	0.158	66.92
ACA-H$_2$O 1	0.5	137.0	903.1	388.79	965.44	54.54	0.307	24.46
ACA-H$_2$O 2	2	198.5	NA$^+$	563.22	1018.96	73.09	0.311	25.09
ACA-H$_2$O 3	4	149.4	876.3	423.97	927.06	62.17	0.287	42.99

$^+$NA – not available.

trogen adsorption measurements applied to the activated carbon aerogels. CA in Table **1** marks carbon aerogel, ACA is activated carbon aerogel. V_{mic} is the volume occupied by micropores. V_{total} and S_{mic} are total pore volume and microporous area of activated carbon aerogels. $\%_{mic}$ is the percentage of microporosity in the samples. ACA-CO_2 and ACA-H_2O refer to the samples activated using carbon dioxide and water, respectively, as activating agents.

It may be seen that the increase of the time of activation of the samples leads to an increase in the total pore volume of the latter, reaching over 1200 mm^3/g after 2 h of activation. Equally, there is an increase in the Langmuir specific surface area from 600 m^2/g in case of non-activated samples to well over 2000 m^2/g in case of samples activated for over 1 h under the CO_2 flow, almost reaching the specific surface area of R-F carbon aerogels [4]; the specific surface area of over 1000 m^2/g was achieved for samples activated under the H_2O flow as seen in Fig. (**2**).
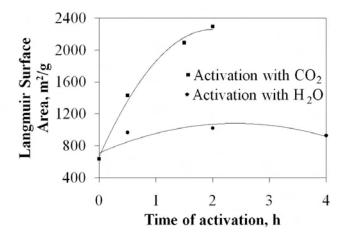

Fig. (2). The Langmuir surface area of the samples under study activated with both water and carbon dioxide.

Judging by the values obtained much higher specific surface area in case of the activation time of over 2 h for CO_2 seem unlikely as the mass loss is already over 65% at this time of activation.

In Fig. (**3**), it may be seen that activation plays a fundamental role in the final appearance of carbon aerogels.
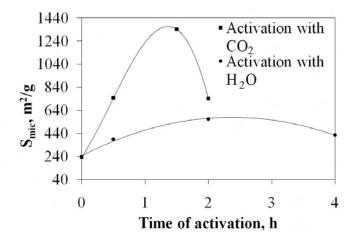

Fig. (3). Microporous area versus time of activation.

During the activation between 60 and 90 minutes, the microporosity of gels reached maximum and samples with a microporosity of over 1400 m^2/g (90% of total area) were formed. However, when the activation time was increased further, samples with a microporosity below 800 m^2/g (less than 50% of microporosity) were formed. The same effect was observed in case of samples activated for 30 minutes or less.

The density of the carbon aerogels activated under CO_2 for 2 h was below 0.16 g/cm^3. The mass loss of the gels was almost 70%. Considering this tendency it is expected that in these conditions activation cannot be carried out for a much longer time than 2 h. In case of activation using H_2O, there is a mass loss which remains constant during the first few hours of activation. After 4 h, the mass loss is over 40% but the maximum specific surface area seems to have appeared within the first 3 h as shown in Fig. (**2**).

Impregnation of Carbon Aerogel

In order to impregnate carbon aerogels with palladium nanoparticles, a quantity of a carbon aerogel was weighed and placed in a high-pressure reactor. Subsequently, $Pd(C_4HF_6O)_2$ was added together with a stirring bar. The reactor was then sealed and placed in a bath at 313 K. The amount of the Pd complex weighed was in the range of 10-15 mass percent of the carbon aerogel mass. CO_2 was then pumped in up to a pressure of 15 MPa and the system was left for 2 h in order to allow the palladium complex time to dissolve. Then, a mixture $CO_2:H_2$ (15:1) was pumped in until the final pressure in the reactor was 18.5 MPa. Then, the system was left to react for 25 minutes before slow decompression. After opening the reactor, the carbon decorated with palladium nanoparticles was obtained and analysed. Fig. (**4**) shows how the carbon network of the aerogel was decorated with palladium nanoparticles after the reduction and decompression in the reactor.

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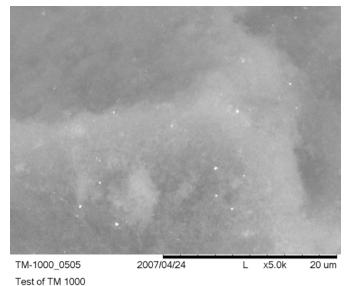Test of TM 1000

Fig. (4). A SEM image of the piece of carbon aerogel impregnated with black palladium.

The catalyst was tested in the reduction of cis-cyclooctene into cyclooctane in supercritical CO_2 having basically a total conversion in the quick reaction. Moreover,

the impregnated piece of carbon aerogel was reused several times in the same reaction reaching the same level of conversion.

CONCLUSIONS

For aerogel preparation, 5-methylresorcinol and its technical mixture, Honeyol™, were shown to be very competitive precursors beside the well-studied resorcinol. An easy control of the gel structure by varying the concentrations of reagents, led to materials with low density and high specific surface area. The preparation of MR-F and H-F aerogels was effective *via* a single-step base-catalyzed synthesis. Supercritical conditions were necessary for drying the wet gel in order to maintain the high porosity of aerogels.

The final properties of gels could also be tailored during pyrolysis and activation as was shown in this study. Samples with high microporosity and large specific surface area as well as samples with a higher value of the specific surface area characterized by being constituted by mesopores mainly were produced. The activation time of over 2 h led to too high mass loss and consequently, a total burn-off of samples when the activating agent was CO_2. In case of using H_2O the mass loss was below 50% during 4 h.

Using a CO_2-soluble palladium salt, the impregnation of carbon aerogels was successfully carried out. The rapid reaction led to samples which were homogeneously decorated with black palladium.

ACKNOWLEDGEMENTS

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PUBLICATION IV

Peikolainen, A-L.; Pérez-Caballero, F.; and Koel, M. Low-density organic aerogels from oil shale by-product 5-methylresorcinol. Oil Shale, 25 (2008), 3, pp. 348–358.

LOW-DENSITY ORGANIC AEROGELS FROM OIL SHALE BY-PRODUCT 5-METHYLRESORCINOL

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The objective of the present work was to prepare organic aerogels using a by-product of oil shale processing as a starting material. Low-density organic aerogels were synthesized via sol-gel polycondensation of formaldehyde (FA) and either 96% 5-methylresorcinol (MR) or the technical mixture named Honeyol™ (H) containing 59.6% of 5-methylresorcinol among other diphenolic compounds, using supercritical CO_2 for drying the gel obtained. Porosity and particle characteristics of MR-FA and H-FA aerogels can easily be controlled by varying the concentrations of precursors and preparation conditions. Less than 4.5-hour drying resulted in MR-FA aerogel characterized by radial shrinkage 2%, density 0.21 g/cm^3 and specific surface area 350 m^2/g. At the same molar ratios H-FA aerogel had 29% shrinkage, 302 m^2/g specific surface area and the density as low as 0.10 g/cm^3.

The preparation techniques and morphology of MR-FA and H-FA aerogels were compared to resorcinol-formaldehyde, phloroglucinol-formaldehyde and phenol-formaldehyde aerogels.

Introduction

Organic aerogels are produced *via* polycondensation of two monomers which form functionalized clusters (sol-gel), and covalent cross-linking of these clusters produces a gel. After processing these gels under supercritical conditions an organic aerogel is obtained. Organic aerogels can further be pyrolyzed to form highly porous carbon aerogels of low density and high specific surface area. Carbon aerogels can be used as membranes, adsorbents and carriers for metal catalysts; they find application in high-energy physics and acoustic technology; low thermal conductivity allows usage as thermal insulators [1]. Carbon aerogels are also promising for electrochemical applications due to their electrically conductive network [2].

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In this paper the preparation of 5-methylresorcinol- formaldehyde aerogel is discussed. 5-methylresorcinol is an alternative precursor for aerogel preparation because its molecular structure is similar to other precursors used for this purpose. Moreover, quicker gelling was expected due to the additional directing methyl group in 5-methylresorcinol molecule compared to the most studied aerogel precursor resorcinol. Methyl substitution also increases hydrophobicity of the gel and thus smaller shrinkage while drying was predicted. In addition, being a by-product in oil shale industry, 5-methylresorcinol is an inexpensive material in the regions where oil shale industry is active.

Properties (density, thermal conductivity, etc.) of an aerogel are dependent on its structure, which can be controlled by the molar ratios of reagents (aromatic compound to formaldehyde, aromatic compound to catalyst and solvent to aromatic compound), the choice of the catalyst and the solvent, gelling conditions and by the way of drying the gel [3–5].

Among other gel drying techniques (conventional drying, freeze-drying), supercritical fluid drying is preferred. At the supercritical state no meniscus is formed between gaseous and liquid phase and capillary pressures within the pores, causing the reduction of porosity or cracking the fragile gel skeleton during drying, are avoided. Resulting densities, specific surface areas and percentages of shrinkage differ accordingly to the fluid used. [6] CO_2 as a supercritical agent is readily available, inexpensive, non-flammable and has low critical parameters ($T_c = 31.1$ °C and $P_c = 7.38$ MPa) [4] that do not decompose sol-gel polymers. Furthermore, its polarity is suitable for removing most of the organic solvents used for such organic polymeric sol-gel preparation [7], and recycling of CO_2 makes it environmentally friendly processing agent.

Experimental

Materials and equipment

5-Methylresorcinol of purity ≥96% was obtained from Carboshale, Estonia; Honeyol™ which is a product of Viru Keemia Grupp, Estonia, was obtained from Department of Oil Shale Technology of Tallinn University of Technology; the catalysts were Na_2CO_3 (purity 99.8%) from Sigma Aldrich Laborchemikalien GmbH, Germany, and KOH from Chemapol Lachema Brno, Czech Republic; formaldehyde was in the form of 35% solution in water, obtained by dissolving paraform in distilled water, when paraform (purity 95%) was from Sigma Aldrich Laborchemikalien GmbH, Germany.

Solvents used were acetone (pure, Petrochemiczne Płock, Poland) and methanol (HPLC reagent, Rathburn Chemicals Ltd., Scotland).

Thermostat for gelation: TECHNE Dri-Block® DB 3A, Spain; supercritical drying was performed on a self-completed equipment consisting of high-pressure pump HPP 4001, Czechia, thermostat: Intersmat IGC 121 C FL,

France, and high-pressure 10-mL cell constructed in laboratory. CO_2 (99.8%) was obtained from Eesti AGA.

Preparation of 5-methylresorcinol-formaldehyde aerogel

The preparation of organic aerogel was started from the gelation of 5-methyl-resorcinol (MR) and formaldehyde: MR was dissolved in distilled water (W), and then the catalyst (Cat) Na_2CO_3 and formaldehyde solution were added. The gelation was carried out in test tubes either at room temperature (25 °C) or at 50 °C. After gelling, the gels were transferred from the test tubes into the acetic acid solution of pH~4 (double-catalyzed synthesis). The next step was solvent exchange – water in the gel was replaced with acetone, and then the supercritical drying followed. The regime of drying the gel with supercritical CO_2 (SCE) comprised of pressurization of CO_2 to 20 MPa at 25 °C, flowing liquid CO_2 through the gel at 12 MPa and 25 °C and super-critical CO_2 extraction at 12 MPa and 50 °C.

In comparison to MR-FA gels, resorcinol- (R), phloroglucinol- (PG) and phenol-formaldehyde gels and single-step acid-catalyzed MR-FA aerogel were prepared under similar conditions.

Preparation of Honeyol™-formaldehyde aerogel

From some trials to prepare Honeyol™-formaldehyde gel (H-FA) similarly to MR-FA gel, it became evident that H-FA needs a stronger basic catalyst than Na_2CO_3 and also higher temperatures for gelling. A homogenous H-FA gel was obtained at 60 °C in the presence of KOH. In this case methanol was used as the solvent instead of water and paraform and KOH were dissolved in methanol. The molar ratios were calculated by the amount of 5-methyl-resorcinol in Honeyol™.

Results and discussion

5-Methylresorcinol is a trifunctional molecule with reaction sites at the 2nd, the 4th and the 6th position of the aromatic ring where the addition of bifunctional formaldehyde results in formation of hydroxymethyl ($-CH_2OH$) groups (Fig. 1). It has been found that the reaction is fast under basic condi-tions (slow in acidic solution) [8], and the kinetics of this reaction is proportional to the size and the valence of the hydrated cation [9]. Na_2CO_3 was used as a basic catalyst in MR-FA aerogels, following Pekala's example of R-FA aerogel preparation [1].

These intermediates further react to form methylene ($-CH_2-$) and methylene ether ($-CH_2-O-CH_2-$) bridged compounds (slow in basic, fast in acidic solution) [8, 10].

Gel formation of MR-FA with optimal molar ratios for obtaining the lowest shrinkage and density (MR/Cat = 60, MR/FA = 0.5 and W/MR = 45) under alkaline conditions and at room temperature occurs within 100 minutes.
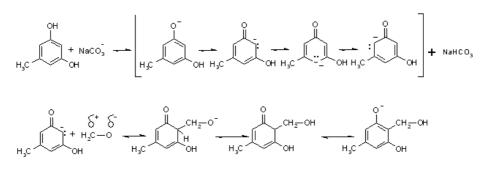
Fig. 1. Addition of formaldehyde to 5-methylresorcinol in the presence of basic catalyst (Na_2CO_3).

Honeyol™ contains dihydroxy benzenes (Table 1) with additional substitutions at the positions where directing groups would affect FA to react on, and with Na_2CO_3 as the catalyst, water as the solvent and room temperature for gelation, the gel could not be obtained.

Although H-FA gel formed after increasing the amount of catalyst, the gel dissolved in acetone during the solvent exchange step. The gel remained intact when methanol, which is also miscible with CO_2, was used for the solvent replacement instead of acetone. Further methanol was used as the original solvent following the examples from the literature [5]. Na_2CO_3 was replaced with stronger catalyst KOH, which was used in smaller amounts. The gelling of the solution with composition H/FA = 0.5, methanol/H = 45, H/Cat = 60 takes at least 8 days at 60 °C, but as the gelling time is strongly dependent on the catalyst amount, the time can be shortened to 1 day by decreasing the ratio H/Cat about 10 times.

By means of IR spectra measurements the gels prepared by single- and double-step catalyzed synthesis were compared (Fig. 2).

Table 1. **Composition of Honeyol™**

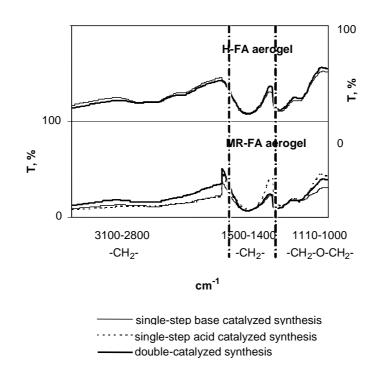| Component	mass fraction, %
Monohydric phenols	**0.8**
resorcinol	5.7
4-methylresorcinol	2.8
5-methylresorcinol	59.6
2-methylresorcinol	1.7
2,5-dimethylresorcinol	8.4
5-ethylresorcinol	9.8
4,5-dimethylresorcinol	7.6
Not identified	3.6
Dihydric phenols	**99.2**

Fig. 2. MR-FA and H-FA aerogels via single- or double-catalyzed synthesis.

In the spectra IR adsorption bands of $-CH_2-$ (2930 cm^{-1} and 1450 cm^{-1}) and $-CH_2-O-CH_2-$ (1100 cm^{-1}) bonds are similar in single-step base catalyzed and single-step acid catalyzed MR-FA aerogels. For the double-catalysed aerogel, the same bonds adsorb less, referring to the effectiveness of the single-step catalysis over the double-catalyzed synthesis. Despite that, from further experiments the single-step acid catalysed reaction was excluded due to unsatisfying homogeneity of the obtained material (under the chosen conditions).

IR spectra of single-step base catalyzed and double-step base-acid catalyzed H-FA aerogels almost overlap (Fig. 2), therefore, the use of only basic catalyst was considered sufficient. The comparison of absorption bands caused by methylene and ether bridges in MR-FA, H-FA, R-FA and PG-FA aerogels is seen in Fig. 3.

Gels from both, di-substituted and tri-substituted aromatic precursors have a similar amount of $-CH_2-O-CH_2-$ bridges between the molecules, showing the equal adsorption band at 1100 cm^{-1}. Methylene bridges at the characteristic wavenumbers (2930 cm^{-1} and 1450 cm^{-1}) show stronger adsorption for R-FA aerogel than for MR-FA, H-FA and PG-FA aerogels. The structure of resorcinol molecule has an unoccupied 5th position, which, we assume, is what makes the close connection between two aromatic molecules *via* $-CH_2-$ bridges preferable compared to tri-substituted molecules where $-OH$ or $-CH_3$ groups at the same positions can be found.
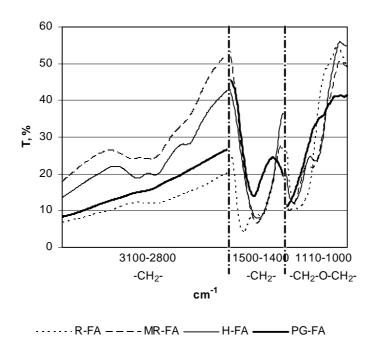
Fig. 3. IR spectra of MR-FA, H-FA, R-FA and PG-FA gels with bands of methylene and ether bridges.

The molar ratios between the precursors (MR/FA, MR/Cat, W/MR or H/FA, H/Cat, methanol/H) were optimized, taking into account the final density, the preparation time and the radial shrinkage during drying. The shrinkage is calculated by the diameters of gel rods before and after drying by the following equation (1):

$$Shrinkage_{radial}[\%] = \frac{\varnothing_{before} - \varnothing_{after}}{\varnothing_{before}} \cdot 100\%. \qquad (1)$$

By excluding the step of catalyzation in acidic media according to the results of IR spectra measurements, the preparation time can be decreased several days.

The number of FA molecules as a cross-linking agent must exceed the number of aromatic molecules to form three dimensional mesoporous material [1], and from this follows that a preferred molar ratio of R/FA is 1:2. On the other hand, formaldehyde remaining in the gel after poly-condensation could induce a collapse of mesoporous structure and decrease the volume of mesopores in the prepared aerogel [11]. From our experiments the MR/FA ratio 1:2 is suitable for MR-FA aerogels (Fig. 4), whose density and shrinkage are the smallest (0.21 g/cm^3 and 2%) compared to aerogels with MR/FA ratios 1:4 and 3:4 (MR/Cat = 60 and W/MR = 45).
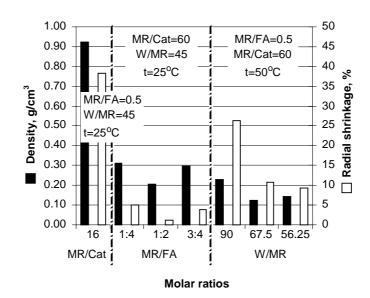
Fig. 4. Densities and radial shrinkages of SCE MR-FA aerogels according to molar ratios.

To strengthen the gel structure before the supercritical drying in order to achieve the minimal shrinkage and the lowest density of the aerogel, the gels were aged 9 days in basic media as it has been suggested for R-FA gels [1]. Later it was found that for MR-FA aerogels with molar ratios MR/FA = 0.5, MR/Cat = 60 and W/MR = 45, curing the gel in basic media for 2 days showed the same results in the aspect of shrinkage and density. Optimal duration of supercritical CO_2 drying according to our research was less than 4.5 hours, as no further decrease in aerogel density or radial shrinkage was detected after a longer processing.

Although our experiments showed that the densities of supercritically dried MR-FA aerogels can be decreased by raising W/MR ratio above 45 (Fig. 4), increasing W/MR to 90, the solid network of the gel becomes too sparse for maintaining the original shape resulting in aerogel with 26% shrinkage having the density 0.23 g/cm^3. Also, an increased W/MR ratio, higher temperature and longer curing time are needed for gel formation. The compromise between the density and the gelling time was made, and the ratio 45 was preferred in experiments.

Phenol gave no homogenous gels at these molar ratios (Phenol/FA = 0.5, W/Phenol = 45, Phenol/Cat = 60) and temperatures. Materials prepared from phenol and FA were either flake-like (preparation at 50 °C) or stiff and hard bulk pieces of novolak (preparation at 90 °C). As gel-like materials were not obtained, the experiments with phenol find no further attention.

R-FA and PG-FA solutions (molar ratios R/FA = PG/FA = 0.5, W/R = W/PG = 45, R/Cat = PG/Cat = 60) resulted in transparent aerogels (ultrafine pore size minimizes light scattering [1]) with densities after SCE drying

respectively 0.22 g/cm^3 and 0.28 g/cm^3. Temperature 65 °C was necessary for synthesizing PG-FA gels because of poor solubility of PG in water. MR-FA gels with MR/Cat ratio 16 were also transparent and having smaller pores than MR-FA gel with MR/Cat ratio 60 (opaque gel), the density and radial shrinkage were affected by drying time at larger scale.

The effect of the supercritical drying is clearly seen in lower final densities compared to the gels dried in ambient conditions (Fig. 5). Drying in ambient conditions makes the gel denser due to greatly reduced porosity (shrinkage 28–45%). PG-FA gel and all the H-FA gels cracked into pieces while drying at room temperature and pressure.

All R-FA, MR-FA, PG-FA and H-FA aerogels consist of nanometre-sized spherical particles and particle clusters (Fig. 6).

Comparing two H-FA aerogels (H/Cat ratios 60 and 6), the decrease of particle and pore sizes is observable. H/Cat ratio 6 leads to transparent gels with particle size 10 nm, while gels with H/Cat ratio 60 are opaque and consist of more than 20 nm sized particles. The pore size distribution for organic aerogels is wide, and no micropores were detected with nitrogen adsorption measurements. PG-FA aerogel consists of less than 10 nm sized particles with PG/Cat ratio 60.

It is known that an increasing amount of catalyst leads to higher density [1], larger total pore volume and specific surface area [11–13] of the aerogel which can be followed in Fig. 7. From the graph it is also seen that the single-step base catalyzed synthesis has proven to be more effective than the double-step catalysis, leading to lower density, larger specific surface area (calculated by Brunauer-Emmett-Teller theory) and higher total pore volume.

The densities of H-FA aerogels are more affected by drying time than MR-FA aerogels (slashes in Fig. 7 legend separate the time, in hours, of each step of CO_2 drying regime). For H-FA density 0.10 g/cm^3 was the lowest achieved with the single-step base catalyzed synthesis (H/Cat ratio 60) with 5 h and 35 min supercritical drying.
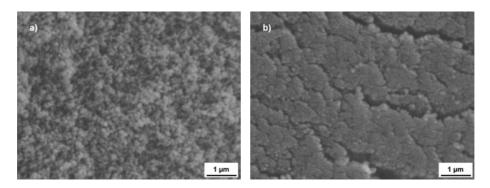

Fig. 5. Effect of supercritical fluid drying on the gel structure. MR-FA gel (MR/FA = 0.75) dried a) by SCE; radial shrinkage 4% and b) in ambient conditions; radial shrinkage 33%.
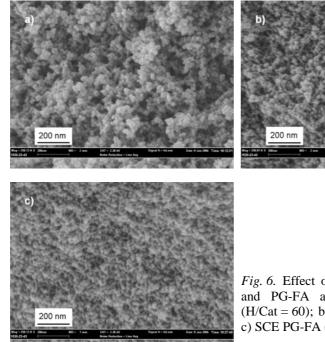
Fig. 6. Effect of catalyst ratio on H-FA and PG-FA aerogels. a) SCE H-FA (H/Cat = 60); b) SCE H-FA (H/Cat = 6); c) SCE PG-FA (PG/Cat = 60).
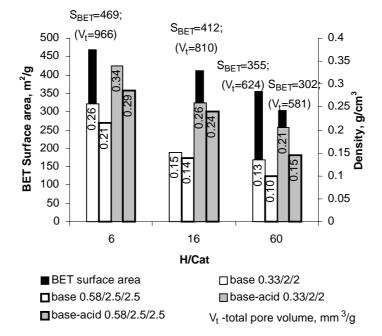

Fig. 7. Influence of catalysts and SCE regime on density, surface area and total pore volume of H-FA aerogels.

The densities and the specific surface areas of aerogels prepared by the double-catalyzed synthesis (R-FA aerogels achieve lower densities at the double-catalyzed synthesis) from different aromatic precursors (resorcinol, 5-methylresorcinol and Honeyol™) with equal molar ratios (R/FA = MR/FA = H/FA = 0.5; W/R = W/MR = Met/H = 45; R/Cat = MR/Cat = H/Cat = 60) and SCE regime are compared in Fig. 8. Temperatures for nitrogen adsorption measurements were chosen based on thermogravimetric analysis (105 °C for R-FA and MR-FA, 180 °C for H-FA).
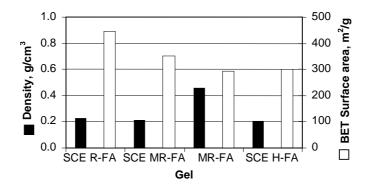

Fig. 8. Densities and BET surface areas of supercritically dried (SCE) R-FA, MR-FA, H-FA aerogels (catalyst ratio 60) and of MR-FA aerogel dried under ambient conditions.

Specific surface area is the largest for R-FA aerogel (455 m^2/g) because the gel consists of small, 7–10 nm sized particles as was discussed above, but as was seen in Fig. 7, it was possible to make an aerogel with the similar specific surface area – 469 m^2/g also from Honeyol™. Specific surface area of the gel is decreased considerably when drying is carried out at ambient temperature and pressure.

Conclusions

For aerogel preparation, 5-methylresorcinol and its technical mixture Honeyol™ are very competitive precursors beside well-studied resorcinol allowing to control the gel structure easily by the same techniques, resulting in very similar characteristics: the lowest density achieved for MR-FA aerogel is 0.21 g/cm^3 and for H-FA 0.10 g/cm^3. Preparation of MR-FA and H-FA aerogels is effective *via* the single-step base catalyzed synthesis requiring at least 10 times larger amount of catalyst than R-FA and PG-FA for gelation. Acid catalyst does not contribute to strengthening the gel structure and does not lead to desired lower densities. Supercritical condi-

tions are necessary for drying, especially for Honeyol™-FA gels, however, drying times for MR-FA and H-FA for obtaining aerogels with previously mentioned densities are extremely short: 4.33 h for MR-FA and 5.58 h for H-FA gel.

Acknowledgements

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PUBLICATION V

Method for preparation of organic aerogel gels

Type	Invention
Author	**Anna-Liisa Peikolainen, Fernando Perez, Mihkel Koel**
Owner of the property (institution)	Tallinn University of Technology

Priority application

Priority date	26.06.2007
Priority number	EE200700032
Classification	International (IPC)
Country	Estonia
Status	Valid

ABSTRACT:

Method of preparation of low density aerogel using formaldehyde and the technical mixture of 5-methylresorcinol as a starting material and methanol as a solvent. Gel is dried by using extraction with supercritical fluid. The by-products from oil shale processing like HoneyolRM can be used as the technical mixture of 5-methylresorcinol. Pyrolysing the aerogel prepared in inert atmosphere of Nitrogen the carbon aerogel will be obtained.

PUBLICATION VI

Pérez-Caballero, F.; Peikolainen, A-L.; Uibu, M; Herbert, M.; Galindo, A.; Montilla, F.; Koel, M. *Oil Shale Phenolic Derived Aerogels as supports for Palladium Nanoparticles.* The Oil Shale Journal. Accepted.

A. Laigo , 1944

03.10.2008 Nr. 22/08

Dear F. Perez-Caballero,

I hereby inform you that your paper "OIL SHALE PHENOL-DERIVED AEROGELS AS SUPPORTS FOR PALLADIUM NANOPARTICLES "has been accepted for publication in journal Oil Shale.

Yours sincerely

Meelika Nõmme
Executive Editor

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- Pérez-Caballero, F.; Peikolainen, A-L.; and Koel, M. "Preparation of nanostructured carbon materials". Proceedings of the Estonian Academy of Sciences (**2008**) 57, 1, 48–53

- Pérez-Caballero, F. et al. "Oil Shale Phenolic Derived Aerogels as supports for Palladium Nanoparticles". The Oil Shale Journal. Accepted.

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- Patent from "Tallinn University of Technology". Authors: A-L. Peikolainen, F. Pérez-Caballero and M. Koel. EE200700032. 26.06.**2007**

- Book Chapter: Organic aerogels as resource for porous carbon material. Authors: Perez-Caballero, F.; Peikolainen, A-L.; Koel, M.; White, R.J.; and Clark, J.H. Accepted for a Langmuir **2009** upcoming publication.

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