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Organic Aerogels Based on 5-Methylresorcinol

ANNA-LIISA PEIKOLAINEN

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TALLINN UNIVERSITY OF TECHNOLOGY
Faculty of Science
Department of Chemistry

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Supervisor: Lead Research Scientist Dr. Mihkel Koel, Department of Chemistry, Tallinn University of Technology

Opponents: Prof. Dr. Irina Smirnova, Institute of Thermal Separation Processes, Hamburg University of Technology, Germany

Prof. Dr. Heikki Tenhu, Department of Chemistry, University of Helsinki, Finland

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any academic degree.

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ANNA-LIISA PEIKOLAINEN

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications which are referred to by Roman numerals in 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.- *Micropor Mesopor Mat* 2008, 108, 230-236.

II Peikolainen, A.-L., Pérez-Caballero, F., Koel, M. Orgaanilise aerogeeli valmistamise meetod (Method for preparation of organic aerogel gels). Patent EE200700032A (2007) from Tallinn University of Technology.

III Peikolainen, A.-L., Pérez-Caballero, F., Koel, M. Low-density organic aerogels from oil shale by-product 5-methylresorcinol.- *Oil Shale* 2008, 25, 348-358.

IV Pérez-Caballero, F., Peikolainen, A.-L., Koel, M., Herbert, M., Galindo, A., Montilla, F. Preparation of the catalyst support from the oil shale processing by-product.- *Open Petrol Eng J* 2008, 1, 42-46.

V Peikolainen, A.-L., Volobujeva, O., Aav, R., Uibu, M., Koel, M. Organic acid catalyzed synthesis of 5-methylresorcinol based organic aerogels in acetonitrile.- *J Porous Mat* 2011, DOI: 10.1007/s10934-011-9459-8.

OTHER PAPERS IN RELATED FIELD

VI Pérez-Caballero, F., Peikolainen, A.-L., Koel, M. Preparation of nanostructured carbon materials.- *P Est Acad Sci* 2008, 57, 48-53.

VII Pérez-Caballero, F., Peikolainen, A.-L., Uibu, M., Herbert, M., Galindo, A., Montilla, F., Koel, M. Oil-shale phenol-derived aerogels as supports for palladium nanoparticles.- *Oil Shale* 2009, 26, 28-39.

VIII Book chapter: F. Pérez-Caballero, A.-L. Peikolainen, M. Koel, R. J. White, V. Budarin, J. H. Clark. Organic aerogels as precursors for the preparation of porous carbons. *In:* Progress in porous media research/ K. S. Tian, H.-J. Shu (editors). New York: Nova Science Publishers, Inc., 2009, 419-459.

IX Palmre, V., Lust, E., Jänes, A., Koel, M., Peikolainen, A.-L., Torop, J., Johanson, U., Aabloo, A. Electroactive polymer actuators with carbon aerogel electrodes.- *J Mater Chem* 2011, 21, 2577-2583.

X Kaasik, F., Torop, J., Peikolainen, A.-L., Koel, M., Aabloo, A. Carbon based electrode material for EAP actuators.- *P Soc Photo-Opt Ins (Proc SPIE)*, 2011, 7976, 79760O-1-79760O-8.

THE AUTHOR'S CONTRIBUTION

I The author participated in discussions and synthesized organic aerogels.

II The author carried out the experiments and wrote the patent.

III The author planned the experiments, synthesized organic aerogels and wrote the manuscript.

IV The author planned the experiments on organic aerogels, carried out the synthesis and wrote the major part of the manuscript.

V The author planned the experiments, synthesized organic aerogels and wrote the main part of the manuscript.

VI The author prepared organic aerogels and wrote a part of the manuscript.

VII The author participated in discussions.

VIII The author made a major contribution to writing the manuscript.

IX The author participated in discussions and synthesized carbon aerogels used in the experiments.

X The author participated in discussions and synthesized carbon aerogels used in the experiments.

ABBREVIATIONS

5MR	5-methylbenzene-1,3-diol, 5-methylresorcinol 5-metüülbenseen-1,3-diool, 5-metüülresortsinool
ACN	acetonitrile
C	catalyst
dHMBA	2,6-dihydroxy-4-methylbenzoic acid 2,6-dihüdroksü-4-metüülbensoehape
FA	methanal, formaldehyde metanaal, formaldehüüd
H	Honeyol™
IR	infrared
NMR	nuclear magnetic resonance
R	benzene-1,3-diol, resorcinol benseen-1,3-diool, resortsinool
S_{BET}	specific surface area calculated by Brunauer-Emmett-Teller theory
SEM	scanning electron microscopy
SFE	supercritical fluid extraction
UV	ultraviolet
W	solvent (water)

INTRODUCTION

Aerogels are highly porous low-density solids. Microscopically, they are composed of sparsely packed nanometer sized particles forming an open porous structure; pores filled with air. Typically, aerogels are materials with large specific surface areas and high pore volumes. The morphology of the material is tunable on the nanometer scale by choosing suitable concentrations of reagents for the gel synthesis, and aerogels with defined structure can be prepared.

Organic aerogels represent an interesting class of materials in themselves, but primarily they are used as the basis for the preparation of materials known as carbon aerogels. Carbon aerogels are valuable materials due to their extremely high porosity and very large specific surface area (the highest specific surface area of carbon aerogel found in the available literature was 3200 $m^2 g^{-1}$) [1]. Their structure of interconnected pores allows them to be used as adsorptive materials [2,3,4] and for hydrogen storage [1]; when doped with precious metal, carbon aerogels become catalyst carriers [5,6,VII]. Carbon aerogels are electrically conductive and can be used as electrodes for electrical double-layer capacitors [7,8], fuel cells [9,10] and electrical actuators [IX,X].

The most commonly used precursors to generate the gel state are formaldehyde (methanal, FA) and resorcinol (benzene-1,3-diol, R) or its derivatives, but may also be prepared from the aqueous gelation and self-assembly of biomass derived polysaccharides. The present work is focused on 5-methylresorcinol (5-methylbenzene-1,3-diol, 5MR) as the precursor for obtaining organic aerogels. This choice was based on two aspects. First, 5-methylresorcinol has a molecular structure similar to resorcinol, having three potential reaction sites in the aromatic ring: positions 2, 4 and 6, but unlike resorcinol, the methyl substitution in the ring position 5 was expected to increase the *ortho-* and *para-*directing properties of substituents and lead to faster polymerization compared to resorcinol. A study by Mitsunaga *et al.* [11] on the reactivity of different phenolic compounds with formaldehyde predicted reactivity more than ten times higher to 5MR than resorcinol. However, having similar molecular structure to resorcinol, many similarities were expected in the gel formation behavior.

The second reason for choosing 5MR as a precursor is its origin. 5MR used in this study was obtained from the local oil-shale industry where it is available as a by-product of oil shale processing. In Estonia, oil-shale is the most important local solid fossil fuel, being a major source of energy, ca. 95% [12]. Fuel and crude oil production generate a remarkable amount of by-products. Oil-shale processing by-products such as phenolic mixtures have been used as raw material in the chemical industry only moderately (less than 8 %) [13]. Alkylresorcinols find application in pharmaceuticals, cosmetics, dyes, high value photoactive resins and novolacs in the electronics industry, as food additives, biocides, fungicides, additives in the plastic industry as well as UV protectors, antioxidants, and stabilizers in the rubber industry. [14]

This thesis contains a literature overview that highlights different aspects of organic aerogel preparation such as gel formation chemistry, alternative precursors, catalysts and solvents, and the tailoring of the aerogel structure. The experimental part of the research on 5-methylresorcinol based aerogels is divided here into three parts. In the first part, a known procedure of aerogel preparation is adapted to a 5-methylresorcinol-formaldehyde aqueous system [I,III,IV]. In the second part, a mixture of various alkylresorcinols is used instead of pure 5-methylresorcinol and a non-aqueous solvent as an alternative [II,III,IV]. The third part is focused on 5-methylresorcinol based aerogels prepared without using special inorganic catalysts but an acidic comonomer instead, and a non-aqueous solvent [V].

AIMS OF THE STUDY

Alongside the focus to search the possibilities of producing aerogels from oil-shale phenols, the aim of this work was to demonstrate the performance of oil-shale origin 5-methylresorcinol as the precursor for aerogel preparation. The emphasis was placed on the following:

- presenting the tunability of the morphology of 5-methylresorcinol based organic aerogels, and finding the correlations between the structural properties and the concentration of components

- showing the potential of a technical, unpurified mixture of alkyl-substituted benzene-1,3-diols as an alternative raw material for aerogel production

- developing an aerogel preparation methodology targeting a simple and fast aerogel production route, which is based on the results of the chemical structure analyses

1 LITERATURE OVERVIEW

The history of aerogels began in 1931 when S.S. Kistler verified his hypothesis that a gel was composed of the solid and liquid phase, independent of each other, and that the liquid in a “jelly” can be replaced by a gas with little or no shrinkage. Evaporation of liquids from gels resulted in large capillary pressure within the pores due to surface tension caused by the receding meniscus, which led to greatly reduced porosity and even cracking of the fragile gel skeleton. Kistler showed that removing the solvent from the gel without two phases present at any time can be carried out via the critical state of the solvent. A liquid is held under pressure always greater than the vapor pressure and temperature higher than the critical temperature and the supercritical fluid will be transformed into a gas. [15] From the moment of this realization, the research on the field of aerogels was focused on possible applications and more economic production routes.

Aerogels can be classified as inorganic and organic aerogels depending on the precursor material. The latest research direction though is the hybrid of both. [16,17] Among organic aerogels the preparation procedure introduced by R.W. Pekala in 1989 [18] is the most studied one being the basis of the generation of organic aerogels. The gel was prepared from resorcinol and formaldehyde and mixed in a 1:2 molar ratio. Deionized water was used as a solvent to control the final gel concentration. After forming a homogeneous solution, sodium carbonate was added and the mixture was cast into the desired shape at temperatures in the range of 70ºC to 100ºC. A minimum of 36 hours were required for necessary cross-linking of the gel, however, longer curing time (48 h-8 days) was found preferable. The gel formed was then acid washed to remove the sodium salts and to promote further cross-linking of the gel, which could impart stability to the gel structure. Prior to drying, the aqueous solvent in the pores of the gel was exchanged for acetone and the following critical point CO_2 drying led to low density organic aerogel. [18]

1.1 Gel formation chemistry

The gel formation chemistry of 5-methylresorcinol and formaldehyde is expected to be similar to R-FA gel formation due to their similar molecular structure. Nevertheless, the methyl group in position 5 could have an important effect on the course of polymerization due to its directing properties or as a potential steric hindrance to two reactive sites of the aromatic ring. Below are the main aspects known for resorcinol-formaldehyde gel formation and suggestions on how it might be in the case of 5MR-FA gels.

Because of the electron donating and *ortho-/para*-directing effect of the hydroxyl groups, resorcinol served as a trifunctional monomer capable of adding formaldehyde in the ring positions 2, 4 and/or 6. Under alkaline conditions, the reaction between resorcinol and formaldehyde led to the formation of addition and condensation products, during which the pH decreased as increasing numbers of hydroxymethyl (-CH_2OH) groups were formed [19]. These intermediates further reacted to form a cross-linked polymer network (Figure 1-1).

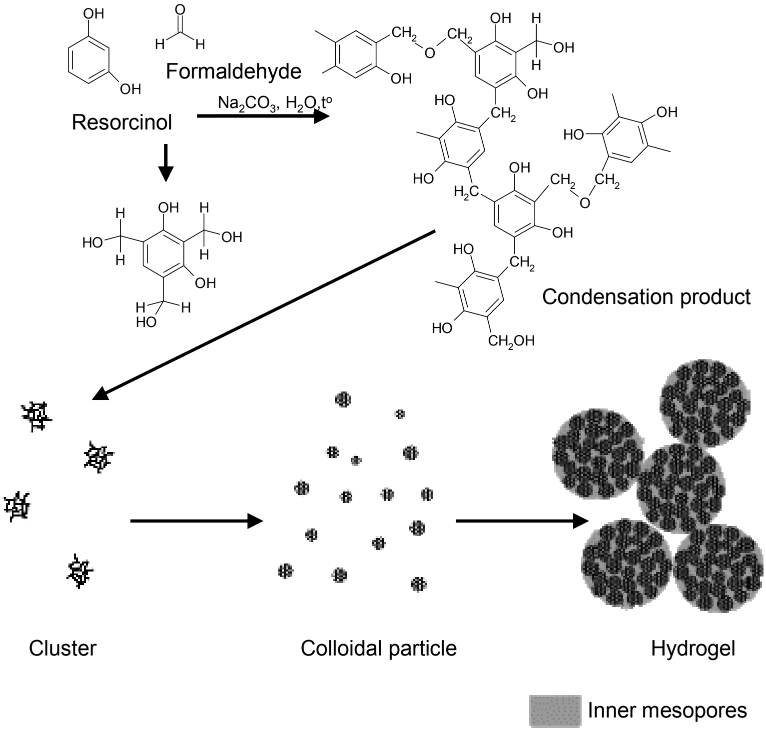


Figure 1-1 Schematic diagram of the sol-gel polycondensation of R-FA solution under alkaline conditions (adapted from [20] and [21])

The two major reactions included the formation of hydroxymethyl (-CH_2OH) derivatives of resorcinol and the condensation of the hydroxymethyl derivatives to form methylene (-CH_2-) and dimethylene ether (-CH_2-O-CH_2-) bridged compounds. [21,22] According to nuclear magnetic resonance (NMR) studies, the preferred site for formaldehyde addition was position 4 with the ratio of 4-hydroxymethyl to 2-hydroxymethyl groups being more than 6:1. The content of hemiformal was detected only in the earliest period of the reaction, but it was found to decrease rapidly and it disappeared after the first hours of the reaction. [23]

Comparison of the reaction rates of various phenolic compounds with formaldehyde in aqueous solution showed a higher reaction rate for 5-methylresorcinol anion than for resorcinol anion with values 2.30E+03 and 1.41E+02 L mol^{-1} h^{-1}, respectively. [11] A strong correlation was observed between the reactivity per reactive site and the average charge per reactive site giving phenol anion as the least reactive species in the row of three the reaction rate 5.13E-02 L mol^{-1} h^{-1}.

The reactivity of 5-methylresorcinol and resorcinol towards polycondensation with formaldehyde has been studied by Christjanson et al. [24] who observed the formation of phenolic resins with NMR spectroscopy. The resin preparation conditions were somewhat different compared to aerogel preparation and a small contradiction between the published results on resin and aerogel polymerization can be found. In the phenolic resin formation, the homocondensation of hydroxymethyl substituted 5-methylresorcinol tended to form a methylene-bridged rather than dimethylene ether-bridged network. [25] The condensation of hydroxymethyl phenols under different catalytic conditions showed that in alkaline conditions, neither the dimethylene ether bridges nor hemiformals were present. The above mentioned groups, however, were formed in the case of non-catalyzed and acid-catalyzed reactions. [26] The reaction rate constants of co-condensation products of *ortho*- and *para*-hydroxymethyl phenols with R or 5MR based on the decrease of -CH_2-OH percentage, were found to be higher for resorcinol. However, if the hydroxymethyl phenols were in the reaction with the mixture containing both R and 5MR, the amount of methylenes linked to R was lower, showing that the reaction with 5MR was preferred. [24] 5MR was very reactive towards formaldehyde and it promoted the formation of dimethylene ether-bridged hydroxymethyl phenols which, at high temperature, released formaldehyde forming then methylene bridges instead. In addition to this, it was found that in resole wood adhesives with phenol/formaldehyde ratio below 0.47, the remaining formaldehyde in alkali-promoted curing process was bound in functionalities, and did not increase its emission. [25]

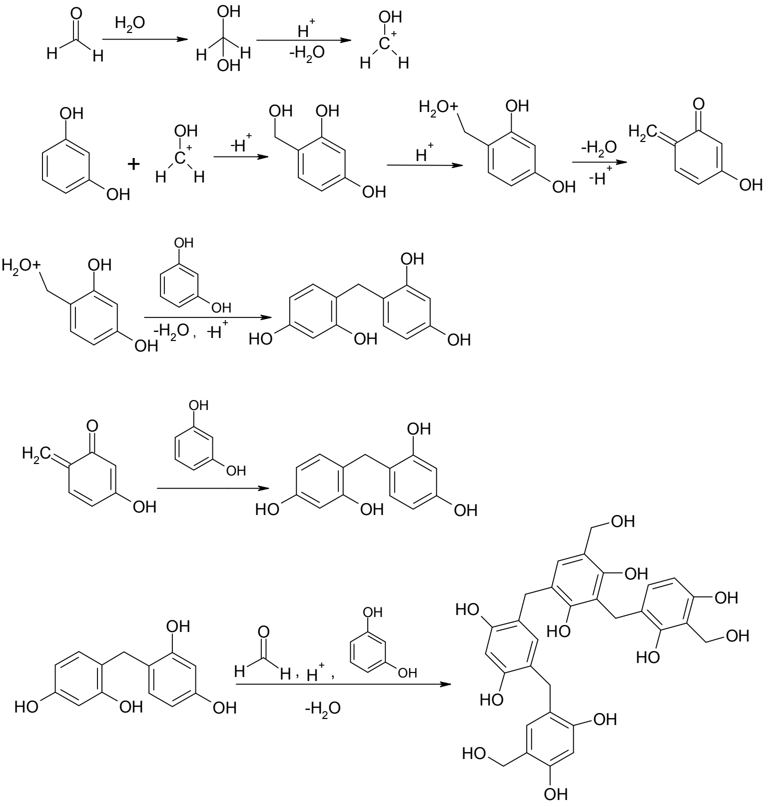


Figure 1-2 Proposed mechanism of resorcinol-formaldehyde polymer formation under acidic conditions [27,28]

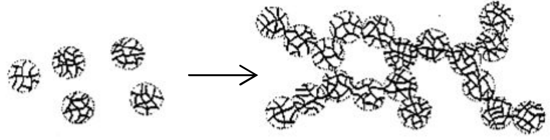
Figure 1-2 summarizes a proposed mechanism for the acid-catalyzed gelation of resorcinol with formaldehyde. Protonation of formaldehyde was followed by nucleophilic attack by the π-system of resorcinol leading to hydroxymethylation. Subsequently, protonation of a hydroxymethyl group formed $-OH_2^+$, a good leaving group that may cleave either unimolecularly, leading to *ortho*-quinone methide-type intermediates, or bimolecularly after direct attack at the $-CH_2OH_2^+$ carbon by the π-system of another resorcinol molecule. The latter process resulted directly in $-CH_2-$ bridge formation between phenyl rings. The mechanism of dimethylene ether bridge formation has not been described for acid-catalyzed reaction. [28]

1.2 Sol-gel process

A sol is a fluid colloidal system where the molecules or the polymolecular particles dispersed in a medium have, at least in one direction, a dimension roughly between 1 nm and 1 µm, or that, in a system, discontinuities are found at distances of that order. A gel is a non-fluid colloidal network or polymer network that is expanded throughout its whole volume by a fluid. Sol-gel process is a process through which a network is formed from a solution by a progressive change of liquid precursor(s) into a sol and to a gel [29], typically at low temperature (T<100°C). [30]

It has been described that in some cases, the macromolecules and the solvent were mixed at a molecular scale, and the gel was made of a single phase that was locally not different from a solution (Figure 1-3b). In many instances however, the gel was a biphasic system, as it was made of a solid polymer skeleton with the liquid phase filling the structure, which was of very complex morphology and comprised of particles with dimensions in the nanometer range (Figure 1-3a). The latter gels were sometimes referred to as being colloidal and the former as being polymeric. The network of colloidal particles linked together has often been referred to as a string-of-pearls type morphology, whereas polymeric gels have been defined as three-dimensional networks of linear or branched polymer chains linked together in random spider-web morphology. [31,32]

a) Sol-gel transition



b) Solution-gel transition

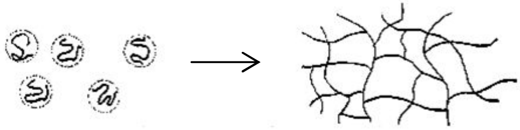


Figure 1-3 Idealized picture of (a) a colloidal gel formed through a sol-gel transition and (b) a polymeric gel formed through a solution-gel transition [31]

Based on fluorescent and light-scattering studies of sol-gel reactions [31] and imaging of aerogels by high resolution transmission electron microscopy [33], the behavior of resorcinol-formaldehyde mixture could have both colloidal and polymeric character depending on the concentration of the catalyst in the mixture. Colloidal gels are of a particular importance in materials science as they are an intermediate step in the sol-gel synthesis of nanostructured materials.

The formation of the microstructure of resorcinol-formaldehyde gels has sometimes been analyzed in terms of a microphase separation [21] and sometimes in terms of an aggregation process [34,35]. According to aggregation theory, the gels form via the formation of colloidal particles that aggregate until they form a space-filling cluster, at which moment a gel is obtained. According to microphase separation, the precursor monomers polymerize and form a branched network in which the polymer and the solvent are mixed at the molecular scale. When the degree of branching and/or the molecular weight increases, the solubility of the polymer in the solvent decreases and the polymer chains progressively fold to form locally denser structures from which the solvent is expelled. [36] Physical arguments have suggested that, in the case of R-FA gels, both aggregation and microphase separation can lead to similar morphologies and those two mechanisms of gel formation should not be regarded as mutually exclusive mechanisms, but rather as two different idealizations of the same complex physical process [36].

1.3 Alternative precursors

Many attempts have been made to decrease the cost of aerogels, improve the methodology of aerogel preparation and obtain aerogels with specific properties. This has been predominantly achieved by using alternative precursors and solvents. Beside resorcinol, organic aerogels have been prepared from other phenolic compounds such as phenol, phloroglucinol (benzene-1,3,5-triol), and cresols (2-methylphenol, 3-methylphenol, 4-methylphenol). Instead of formaldehyde, an alternative cross-linking agent between aromatic monomers has proven to be furfural (furan-2-carbaldehyde). There are examples of phenol-furfural aerogels [37,38,39] and resorcinol-furfural [40] aerogels.

Typical examples are also gels obtained from melamine and formaldehyde [41,42], phenolic resole resin and hydroxymethyl melamine [43], polyurethane [44], and poly(vinyl chloride) [45].

1.3.1 Phenol

Among the variety of phenols, unsubstituted phenol is presumably the most widely used and inexpensive substance, however, its reactivity with formaldehyde is relatively low compared to other phenolic precursors. A significant amount of water must coexist with the phenol and formaldehyde monomer precursors during the synthesis of carbon aerogel precursors, which not only reduces the reaction rate but also limits the maximum reaction temperature. In addition, despite having a hydrophilic hydroxyl group in its structure, it is difficult to obtain hydrophilic colloidal particles from it. If such particles cannot be obtained during gel synthesis, phase separation will occur, which results in the formation of a polymer, which cannot be turned into a carbon aerogel. The strategy has been to adopt synthesis conditions, which allow the colloidal polymers, obtained through the polymerization of phenol and formaldehyde to maintain their hydrophilicity until gel formation is completed (i.e. at a low phenol concentration and a high catalyst concentration). [46]

In the case of a phenolic-furfural system [37,38], the sol-gel polymerization could be conducted in alcohol (e.g., 1-propanol), thereby eliminating the need for a solvent exchange step prior to supercritical CO_2 drying. The resultant aerogels were dark brown in color and could be carbonized upon pyrolysis in an inert atmosphere. The specific surface areas obtained were in the range of 350-600 $m^2\ g^{-1}$ and transmission electron microscopy revealed an interconnected structure of irregularly shaped particles or platelets with 10 nm dimensions. [39]

1.3.2 Phloroglucinol

Phloroglucinol-formaldehyde aerogel is an example of an important simplification of an aerogel preparation process. Using alcohol-soluble phloroglucinol as an alternative precursor, the solvent exchange step was eliminated from the aerogel preparation process. [47] In addition, the enhanced electron density of the phloroglucinol ring promoted faster polymerization compared to phenol and resorcinol.

1.3.3 Cresols and the mixture of alkylphenols

Preparation of aerogels from mixed cresol has lowered the cost of aerogel production. The tunability of specific surface area was moderate and very high catalyst amounts were used [48] (compared to resorcinol), but the largest specific surface areas obtained were relatively competitive. [49] A mixture of cresol and formaldehyde (with up to 70% of cresol) allowed the obtainment of low density (0.57 g cm^{-3}) porous materials even at ambient drying conditions (similarly to resorcinol). [50]

Aerogels from alkylresorcinol or from the technical mixture containing multiple alkylresorcinols have not been reported before. 5-methylresorcinol and its technical mixture however, have been used for solid oligomeric resin preparation. [51] An example of the low density material from the mixture of alkylresorcinols is foam plastic, where the lightweight structure was obtained using a surface active agent and the durability of the foam was achieved by adding powdered boron or aluminum to the mixture. [52]

1.3.4 Melamine

Nitrogen containing monomers are known with melamine-formaldehyde being the most studied system. Melamine-formaldehyde resin may also be employed as a carbon precursor for the preparation of nitrogen-rich macroporous carbon aerogels. Nitrogen rich carbon gives better possibilities for surface modification of the material. [42,53]

1.3.5 Biomass derived polysaccharides

The new class in organic aerogel technology is biomass derived aerogels. Natural polysaccharides such as cellulose, starch, alginate, κ-carrageenan, and chitosan are less energy-intensive aerogel precursor materials compared to phenolic ones. Polysaccharides are known to self associate or order into particular structures, physical forms or shapes upon inducement of an aqueous gel state. Sol-gel polymerization (and ionotropic gel formation) can give also covalently bonded polysaccharide structures.

Biomass derived aerogels have been proposed for use as adsorptive materials. The porous chitosan microspheres having the amine functionality in the polysaccharide framework possess intrinsic catalytic activity, being successfully applied to catalyze the asymmetric aldol reaction [54]. Starch and alginate based aerogels are promising as drug carriers [55]. Electrochemical applications are of interest [56].

In Table 1-1, literature data on organic aerogels from the most popular precursors have been gathered. The range of preparation times, temperatures, specific surface areas and densities are dependent on various aerogel preparation conditions such as precursors and their concentration in the solvent, the type and the amount of catalyst, the solvent, and the drying process efficiency in terms of preserving the original gel structure.

Table 1-1 Alternative precursors for organic aerogels and their structural parameters

Aerogel precursor	Preparation time, days	T, °C	S_{BET}, m^2 g^{-1}	Density, g cm^{-3}	Reference number
resorcinol	12	50-90	160-850	0.03-0.52	[18, 57, 58, 59]
phenol	7-12	80-90	260-520	0.13-0.62	[37, 60]
cresol	7	90	230-630	0.06-0.37	[48, 61]
phloroglucinol	2-11	90		0.01-0.04	[62]
melamine	8-38	25-95	850-1000	0.10-0.75	[41,63]
cellulose	8-9	rt-110	150-400	0.01-0.85	[64, 65, 66, 67]
chitosan	1-3	rt	110-845	nd	[68, 69, 70, 71]
alginate	2 (8)	rt (rt or 4)†	220-570	0.13	[68, 72, 55]
κ-carrageenan	2	80 (5) †	200	nd	[68]
starch	3 (9-13)	60-95 (4) †	180	nd	[55, 73]

rt- room temperature; nd- no data;
†- “precursor dissolving temperature” (“gelation temperature”)

1.4 Solvents and supercritical drying

In order to obtain aerogels with low density and high specific surface area, the solvent in the gel pores has to be removed without destruction of the solid gel structure. Evaporation of the solvent generates capillary pressure in the pores due to surface tension of the fluid causing shrinkage and even cracking of the material. It has been found that under supercritical conditions the fluid can be removed from the material without surface tension, leaving the porous structure of the material unharmed. [74] On Figure 1-4, a phase diagram is given with the scheme of drying: the liquid (point A) is first taken to the supercritical state by raising the pressure above the critical pressure (P_c), and then the temperature above the critical temperature (T_c) (point B). The gas phase is achieved by decreasing the pressure to atmospheric pressure followed by lowering the temperature to the ambient temperature (point C). [75]

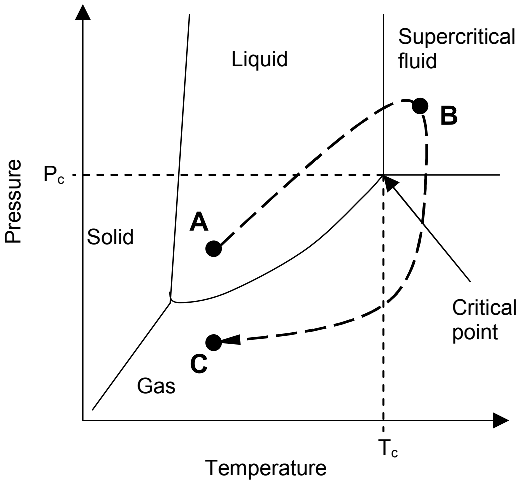


Figure 1-4 Phase diagram depicting the scheme of drying over the supercritical state of the fluid [75]

Water above its critical parameters ($T>T_c$, $P>P_c$) is very reactive and direct supercritical drying decomposes the gel. Therefore, one approach is that after the gel has been formed, the water in the pores is replaced with another solvent that has either lower critical parameters (acetone [76], alcohol [77]) to be dried directly via supercritical state, or is miscible with the fluid that is used later for supercritical drying of the gel. In the case of resorcinol-formaldehyde hydrogel, the water is typically exchanged for acetone or alcohol, after which the solvent is removed using CO_2 extraction, followed by venting the liquid CO_2 from the pores of the gel via supercritical state. Carbon dioxide is often the fluid used for supercritical drying because of its low critical parameters (T_c=31.13°C; P_c=73.75 bar, see Table 1-2). It is also readily available and inexpensive, non-flammable, non-toxic, reusable, environmentally friendly, no CO_2 residues are left in the treated medium, and the properties of the supercritical fluid can be finely tuned by varying the temperature and pressure [78]. The polarity of CO_2 is suitable for removing most of the organic solvents used for the sol-gel preparation of organic polymers [79]. However, for removing water CO_2 is not suitable and in order to use supercritical CO_2 drying, water in the gel pores is replaced with another solvent miscible with CO_2.

Table 1-2 Critical point parameters (T_c- temperature, P_c- pressure) of selected fluids [80]

Fluid	T_c, °C	P_c, bar
Water	374.14	220.6
Carbon dioxide	31.13	73.75
Methanol	239.5	80.84
Acetone	235.1	47.0
Acetonitrile	272.5	48.5

The process of solvent exchange is time consuming, being limited by the speed of diffusion, and because it is crucial to remove the water to succeed in drying (resulting in low shrinkage), a considerable amount of replacement solvent is consumed which later requires energy for its recovery or disposal. Thus, an alternative strategy is to prepare the gel directly in the suitable solvent. For example, organic gels prepared in alcohol [81], acetone [82,83] and acetonitrile [28] have been reported.

According to Kobayashi [84], under acidic conditions, resorcinol-acetone copolymer can be prepared but is not obtained in the form of the gel, but it is obtained as a precipitate.

Mulik *et al.* synthesized resorcinol-formaldehyde gels in acetonitrile, which they exchanged for acetone, followed by supercritical CO_2 drying. [28,85] In accord with the study of A.W. Francis on phase equilibria of ternary systems with liquid carbon dioxide, acetonitrile and water [86], it is possible to apply CO_2 extraction directly to the gel that contains acetonitrile. This has been done by Willey *et al.* [87], who, in order to dry the humic acid gel, replaced the original solvent (water) in the gel by acetonitrile prior to supercritical CO_2 drying.

Acetonitrile is a polar aprotic solvent and does not form hydrogen bonds. As an advantage, in polar aprotic solvents most anions are much less solvated and hence more reactive than in hydrogen bond forming solvents. [88]

Despite the capillary forces not being present while the solvent removal goes via the supercritical state, the shrinkage of the aerogel monolith still occurs. One reason may be related to incomplete solvent exchange from the small pores and capillary forces, which are present to some extent. However, Zhang *et al.* have explained the shrinkage that occurs during solvent exchange and supercritical drying with the change in the hydrophilicity of the solvent media. There were said to be strong hydrophilic interactions between discrete gel particles, and between the solvent and discrete gel particles. In the supercritical drying process, displacing acetone with carbon dioxide and complete removal of solvent causes the destruction of hydrophilic interaction between acetone and the polymer matrix and of hydrophobic interaction between CO_2 and hydrophobic groups in the polymer matrix, respectively, which in turn cause volume shrinking of gels. [89]

1.5 Catalysts

In aerogel preparation, both base and acid catalysis may be used to promote the cross-linking reaction between the monomers. Sodium carbonate has extensively been used as a catalyst due to its availability, sufficient catalytic properties and not a very high chemical hazard. Nevertheless, there are several alternatives.

1.5.1 Base catalysts

The reaction mechanism and kinetics are influenced by the size and valence of the cation in the base composition. [90]

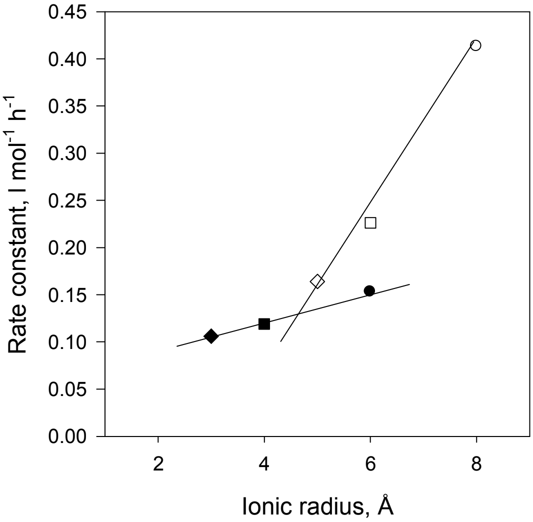


Figure 1-5. Influence of the size of hydrated cations on the rate of disappearance of formaldehyde: ♦ KOH; ■ NaOH; ● LiOH; ◊ Ba(OH)$_2$; □ Ca(OH)$_2$; ○ Mg(OH)$_2$ [90]

The rate constant k for formaldehyde disappearance was related to the ionic radius of the hydrated cation; the sequence: $k_{Li+} > k_{Na+} > k_{K+}$ and $k_{Mg2+} > k_{Ca2+} > k_{Ba2+}$ can be estimated on Figure 1-5. Divalent cations led to higher rates of formaldehyde disappearance compared to the monovalent cation, but the relationship for both monovalent and divalent cations is linear. [90]

The influence of the base catalyst type on the porosity of R-FA carbon aerogels has been studied by Horikawa *et al.* [91] via small-angle X-ray scattering. Only minimal difference in micropore (pores with diameter <2 nm) volumes was observed as a product of different catalyst species and ratios. A greater influence on the mesopore (pores with diameter 2-50 nm) volumes of these aerogels was observed, demonstrating a strong dependency on the catalyst species and ratio (molar ratio of resorcinol to catalyst) employed.

1.5.2 Double-step base-acid catalysis

After obtaining a gel under basic conditions, curing in acidic media has been proposed as the next step [62] to promote further cross-linking of the monomers to obtain gels that have stronger structure, thus allowing less shrinkage during the drying and resulting in aerogels with lower densities compared to those prepared without the step of curing in acidic media. It has been shown that basic media activates *ortho*- and *para*- sites of the phenolic compound and leads to fast formation of hydroxymethyl substitutions (Figure 1-6a). After this process, the formation of clusters starts slowly with hydroxymethyl groups forming dimethylene ether and methylene bridges between aromatic molecules. The second process occurs faster if reaction is performed under acidic conditions (Figure 1-6b).

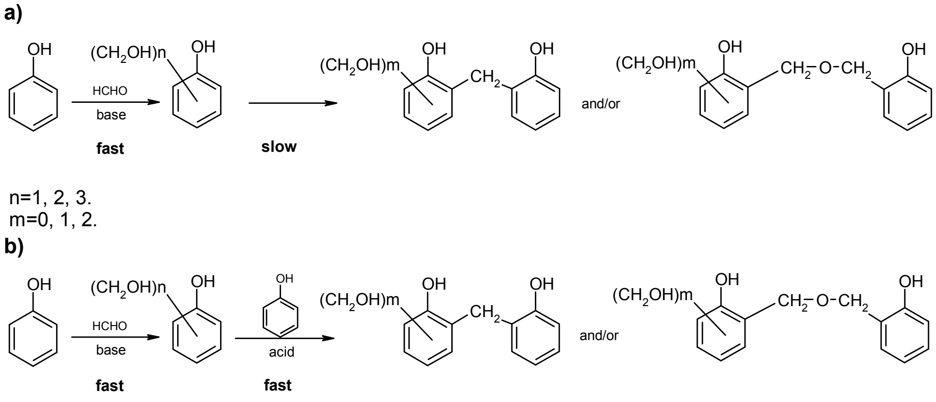


Figure 1-6 Schemes on steps of formation of resole polymers by (a) base catalyzed process and (b) double step process [62]

Curing the gel in dilute aqueous acidic solution also neutralizes the base catalyst and leads to lower inorganic content in the final aerogel product.

1.5.3 Acid catalysts

Base catalysts are typical in aerogel preparation, but in some cases, acid catalysts like HCl or acetic acid have been used for aerogel preparation.

The reaction of R with FA and the subsequent condensation of the resulting hydroxymethyl resorcinol with R, are electrophilic aromatic substitutions, and therefore proceed efficiently by acid catalysis via a convenient one-pot synthetic approach [28]. A HCl-catalyzed gelation process in acetonitrile has been developed and reported. It was completed in about 2 h at room temperature or in 10 min at 80°C. The final aerogels were chemically indistinguishable (by IR and ^{13}C NMR) from typical base-catalyzed samples.

Recently, the same group replaced HCl with hydrated metal ions as Brønsted acids for the catalysis of the resorcinol-formaldehyde gelation in acetonitrile/ethanol, resulting in a type of copolymer with interpenetrating networks of metal oxides and resorcinol–formaldehyde [85].

In order to prevent inorganic impurities, aerogels can be prepared using organic acids. For example, acetic acid [92], oxalic acid and 4-methylbenzenesulfonic acid [93] have been used in aqueous systems as catalysts for aerogel preparation.

1.6 Tailoring aerogel structure

The physical properties of the aerogel are dependent on the structure of the original gel. The size of the particles and pores and the surface area of the aerogel have been tailored by varying the concentrations of the reagents, commonly expressed as molar ratios.

Tailoring of the gel structure could be achieved via altering the molar ratio of aromatic monomer to cross-linking monomer, in the example of the resorcinol-formaldehyde system the ratio of R to FA (R/FA) and aromatic monomer to catalyst (R/C). Further control has been exerted via control of the amount of solvent used, nominally expressed as the percent of the solid fraction, or occasionally as the molar ratio of solvent (W-water) to aromatic monomer (W/R), catalyst to solvent (C/W) or solvent to catalyst (W/C).

1.6.1 Resorcinol-to-formaldehyde ratio

R-FA aerogel prepared under acidic conditions has shown that R/FA ratio does not have a profound influence on the aerogel structure, resulting in the similar shrinkage, porosity, specific surface area and particle diameter for aerogels with R/FA ratio from 0.1 to 0.5. The bulk density however, was the lowest for R/FA molar ratio 0.5, which was more than 20% smaller compared to aerogel with R/FA ratio 0.33. [28]

The molar ratio for optimal cross-linking has been found to be in the range of 0.4 - 0.7, with a 0.5 ratio in the preferred embodiment. [94] Although the specific surface area was independent of R/FA ratio, a strong dependence for mesopore volume and pore size distribution was observed and divided into two groups. Mesopore volume and average pore size were small for R/FA ratios ≤ 0.34, whilst increasing the ratio to values ≥ 0.40 resulted in an increase in the mesopore size. It was assumed that the high amount of formaldehyde remaining in the sol-gel induced a collapse of mesopore structure and decreased the mesopore volume in the resulting aerogel. In the case of systems composed of R/FA ratios = 1.0, the resulting sol did not gel enough to allow for production of porous aerogel material. [94]

In most studies the chosen R/FA ratio is 0.5 when, in order to study the possibilities of tuning the structure, R/C and W/R ratios have been altered.

1.6.2 Resorcinol-to-catalyst ratio

The greatest impact on gel structure has the amount of catalyst used in the polymerization step and is typically expressed as the molar ratio of aromatic compound to the catalyst at a constant volume of water. An increase in the catalyst concentration in the sol led to smaller gel particles, smaller pores and a larger specific surface area [21,57,59,94]. At high catalyst concentration the gel shrank significantly compared to the gel with lower catalyst concentration and the density was also higher. [59,48]

Figure 1-7 summarizes particle formation in a system composed of high and low catalyst concentrations.

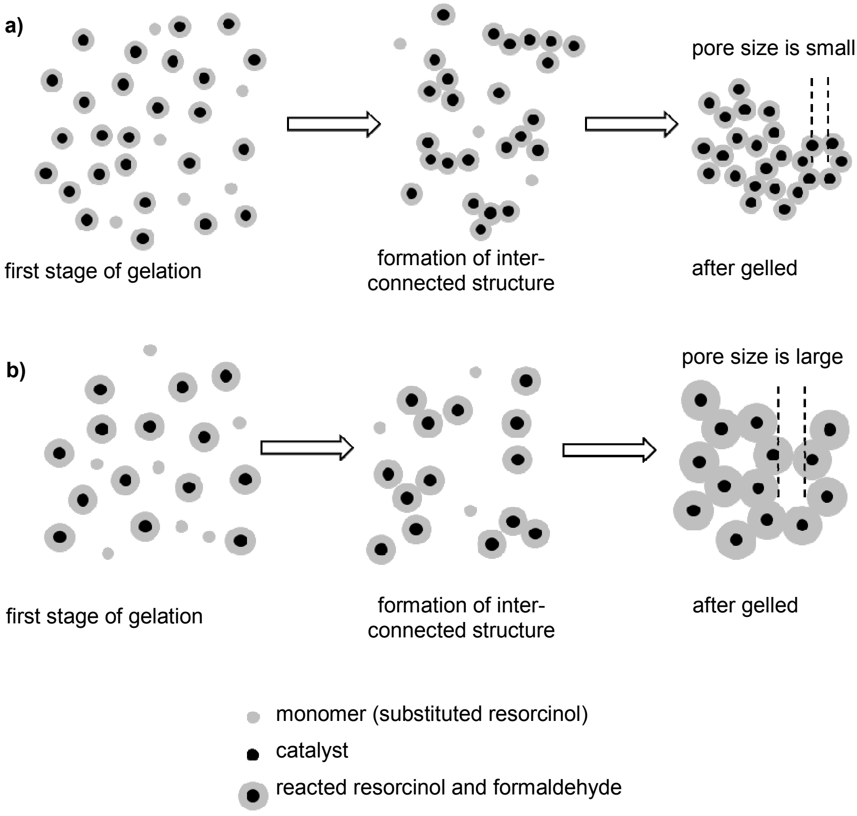


Figure 1-7 Depiction of the effect of R/C ratio on the growth of aerogel particles (a) at high and (b) low catalyst concentration [95]

During the first stage of the gelation process, each colloidal particle grows individually at the catalytic site; subsequent aggregation generates the interconnected structure initially, resulting finally in the cross-linked porous R-FA hydrogel structure. If catalyst concentration is high, particle growth points are densely packed. Thus a small amount of the reactant is consumed per colloidal particle and consequently the size of the particles remains small. Contrasting this, if catalyst concentration is low, particle growth initiation points exist sparsely. Therefore, a large amount of the reactant is consumed per colloidal particle and consequently the particle size increases as a function of decreasing catalyst concentration. Likewise, the pore size becomes relatively small if the catalyst concentration is high and vice versa. [95] Increase of the specific surface area upon increasing catalyst concentration can be explained based on the same model: the particle size becomes smaller and the specific surface area of the aerogel becomes larger. [21,33] The volume of mesopores is influenced the same way: increasing catalyst concentration leads to higher mesoporosity [57]. The presence of micropores in organic aerogels has been found to be insignificant [37,48,57] because, mainly, they are formed during pyrolysis, being present in carbon aerogels. Despite this, the trend is similar: higher catalyst concentration leads to higher amount of micropores. It has been noted, however, that unlimited catalyst concentration increase does not necessarily lead to higher surface areas but changes the structure of the material towards polymeric, leading to much decreased specific surface area with very small total pore volume. [48]

If the size of the colloidal particles formed was much smaller than the wavelength of visible light, transparent hydrogels could be obtained. For catalyst ratios $25 < R/C < 400$, in resorcinol-formaldehyde systems, the resulting gels obtained were transparent. For $R/C \leq 25$, gels became increasingly opaque, frangible and hard. For $R/C \geq 400$, gels were opaque and soft. [94]

Besides affecting the aerogel morphology, the catalyst concentration affects the gel time. Gel time is a time interval from the start of a network-forming process to the gel point. [29] The gel time decreased upon increased catalyst concentration. [96,97] The gel time also depends on the temperature at which the sol was cured. [96,97] The mesoporous properties of R-FA hydrogels however, were not greatly influenced by the gelation temperature. [98]

1.6.3 Resorcinol-to-water ratio

The gel formation may be hindered in a sol too dilute (e.g low R/W ratio). Zhang *et al.* [99] have studied the influence of phloroglucinol content in the sol and its impact on volume shrinkage during drying, specific surface area and pore volume in the resulting porous aerogel products. The gels formed at low reactant concentrations were discrete, with weak junctions existing between particles; such gels collapsed, having significant volume shrinkage when the gel-bound water was replaced with acetone. In contrast, gel networks formed at higher phloroglucinol concentrations were bicontinuous and the gel structure collapse did not occur during the solvent exchange step. Mesopores were formed during the gel formation. At low aromatic compound concentration the mean mesopore size was small compared to higher aromatic compound concentration. Increasing the amount of aromatic compound induced the formation of larger mesopores.

The clear correlation between R/W and the specific surface area of organic aerogels has not been dated, but the pore size has been found to increase with increasing R/W ratio. [94,97] Figure 1-8 depicts the influence of the solid fraction amount on the gel time: at higher values the gelling occurs faster.

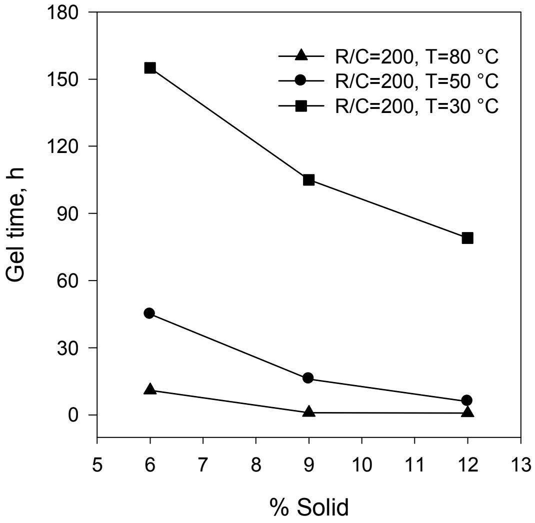


Figure 1-8 Effect of solid fraction of resorcinol on gel time depending on gelation temperature [97]

2 EXPERIMENTAL

This work was carried out step by step and can be divided into three parts. As the first step, a known procedure of aerogel preparation was adapted to a 5-methylresorcinol-formaldehyde aqueous system. In the second part, a mixture of various alkylresorcinols was used instead of pure 5-methylresorcinol and a non-aqueous solvent. The third part is focused on 5-methylresorcinol-based aerogels prepared without using special inorganic catalysts, but instead an acidic comonomer as well as and a non-aqueous solvent.

2.1 Materials and methods

2.1.1 5-methylresorcinol-formaldehyde aerogels

5-methylresorcinol (99.6% and 99.9%) was obtained from Carboshale OÜ, Estonia and Viru Keemia Grupp AS, Estonia; formaldehyde solution in water was either purchased or prepared from paraformaldehyde powder; Na_2CO_3 was used as a catalyst and an aqueous acetic acid solution for the acid catalysis; deionized water was used as a solvent and acetone with technical purity as a solvent for solvent exchange.

The gels were prepared by dissolving 5-methylresorcinol and the catalyst (C) Na_2CO_3 in deionized water (W), then, formaldehyde solution was added. The gelation was carried out in cylindrical test tubes at 25°C via single- and double-catalyzed synthesis routes. After the gel was formed, it was aged 24 h before further processing. In the case of single-catalyzed synthesis, the gel was placed into acetone as the next step to carry out the solvent exchange. Acetone was replaced every 24 h with a fresh one within a minimum of 4 days; every time the volume of acetone was ten times the volume of the gel piece. In the case of double-catalyzed synthesis, the step that followed aging was curing the gel in acidic media for 2 days prior to the solvent exchange step.

2.1.2 Honeyol™-formaldehyde aerogels

Honeyol™ (H), which is a product of Viru Keemia Grupp AS, Estonia, was obtained from the Institute of Oil-Shale at Tallinn University of Technology. The composition of Honeyol™ is given in Table 2-1; KOH was used as a catalyst; formaldehyde solution in methanol was prepared from paraformaldehyde powder. Methanol was used as a non-aqueous solvent.

Honeyol™ was dissolved in methanol, KOH solution in methanol was then added, followed by formaldehyde solution. The molar ratios were calculated by the amount of 5-methylresorcinol in Honeyol™. A homogeneous H-FA gel was obtained at 60°C. The gel obtained was placed directly into the autoclave for drying with CO_2 supercritical extraction.

Table 2-1 Chemical composition of Honeyol™ (fraction 270-320°C) used in the experiment (data provided by Institute of Oil Shale at Tallinn University of Technology)

Monohydroxy benzenes	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%
other	3.6%
Dihydroxy benzenes	**99.2%**

2.1.3 5-methylresorcinol- 2,6-dihydroxy-4-methylbenzoic acid-formaldehyde aerogels

5-methylresorcinol (99.6%) and 2,6-dihydroxy-4-methyl benzoic acid (dHMBA) (>99%) were obtained from Carboshale OÜ, Estonia; formaldehyde solution in water was used and acetonitrile (ACN) was a non-aqueous solvent in the reaction.

Appropriate amounts of the aromatic precursors, 5MR and dHMBA, were dissolved in acetonitrile, and a formaldehyde solution was subsequently added. The molar ratio of aromatic monomers to formaldehyde was fixed at 0.5 and the molar ratio of the solvent (H_2O in FA solution and ACN) to the aromatic monomers was kept at 50. The molar ratio of 5MR to dHMBA (%5MR/%dHMBA) was varied from 90 and 10 mol% (indicated as 90/10) to 25 and 75 mol% (indicated as 25/75) of the total molar amount of aromatic monomers in the sol, respectively. Sol-gel polycondensation occurred at 25°C. After aging the gel for a minimum of 24 h, it was removed from the test tube and placed directly into the autoclave for drying with CO_2 supercritical extraction.

2.1.4 Gel drying regime

An optimized drying regime was used for drying the gels obtained. First, the gel was introduced to liquid CO_2 at a pressure of 200 bars at 25°C for 20 minutes, in order to fill the pores of the gel with liquid CO_2 and mix it with the solvent. The exit valve of the autoclave was then opened and the internal pressure reduced to 100 bars, allowing the liquid CO_2 to flow through the gel at a constant 100 bars at 25°C for 2 or 4 hours (depending upon the volume of the autoclave used) to replace the mixture of CO_2 and the solvent with CO_2. After replacement, the temperature inside the autoclave was raised to 45...50°C and supercritical CO_2 extraction (SFE) was carried out for 2 hours. The extraction was completed by depressurizing the autoclave to atmospheric pressure, and then lowering the temperature in the autoclave to ambient temperature.

2.2 Instrumentation

The thermostat for gelation covered a temperature spectrum of 20-100°C; supercritical drying was performed using either a 10 ml high-pressure cell or a 100 ml autoclave. CO_2 (99.8%) was obtained from AS Eesti AGA.

2.3 Analysis techniques

The gel point was affirmed visually, tilting the sol-filled test tube 45° while observing the movement of the surface of the sol.

The density was calculated as the weight to volume ratio of the solid aerogel monolith. Shrinkage was calculated as a decrease of the cross-sectional area of the cylindrical gel monolith during drying (Eq. 1).

$$Shrinkage, \% = \frac{A_{gel} - A_{OA}}{A_{gel}} \cdot 100 \qquad (1)$$

A_{gel} and A_{OA} are the cross-sectional areas of the gel and the corresponding aerogel, respectively.

The following results were obtained from outside the institute: infrared (IR) spectrometry measurements were carried out in the Department of Chemistry of Tallinn University of Technology; scanning electron microscopy (SEM) analyses were performed in the Department of Material Science and in the Laboratory for Materials Research; the results of nitrogen sorption analysis and thermogravimetric analysis (TGA) were obtained from the Laboratory of Inorganic Materials; nuclear magnetic resonance (NMR) spectra were measured in the National Institute of Chemical Physics and Biophysics. Details can be found in original publications.

The specific surface area indicated as S_{BET} designates the area calculated according to the Brunauer-Emmet-Teller (BET) theory.

3 RESULTS

3.1 5-methylresorcinol-formaldehyde aerogels

3.1.1 Gel formation

The measurements of gel time were performed using visual determination of gel point. Although it is known to give systematically longer gel times compared to rheological measurements, both methods have been found to follow a similar trend. [96]

The suitable monomer ratio (5MR/FA) with respect to fast gelation can be determined on Figure 3-1 where the gel times of 5MR-FA sols obtained at 5MR/C=60 with different 5MR/FA (0.25, 0.5, 0.75) and W/5MR (45, 56.25, 67.5) molar ratio combinations are compared. Sols with W/5MR molar ratio 90 at the given conditions either did not lead to homogeneous gels (within a reasonable time) or the gels formed did not maintain their form in order to be processed further.

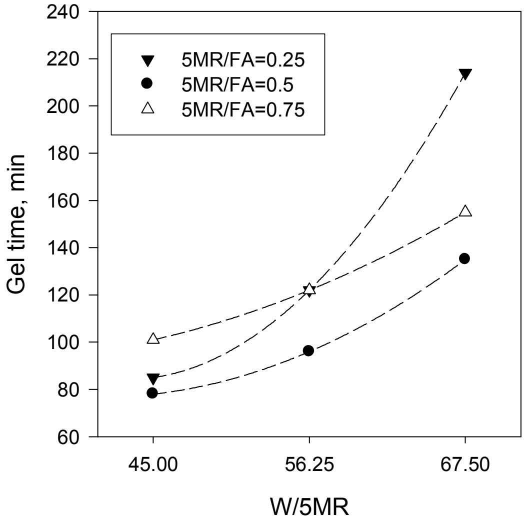


Figure 3-1 Gel time for sols with 5MR/C molar ratio 60 depending on W/5MR and 5MR/FA ratios (for visual clarity, the lines are drawn through the data points)

From the figure it can be seen that the gel time increases while decreasing the monomer concentration. The shortest gel time is achieved at W/5MR ratio 45 at every chosen 5MR/FA value. Compared to other 5MR/FA ratios, 0.5 appears to have an advantage in gel formation having the shortest gel time at every tested W/5MR ratio.

The density of the aerogel is directly related to the W/5MR ratio in the sol: lowering monomer concentration in the sol allows for obtaining materials with lower densities after removal of the solvent- Figure 3-2. In the case of the double catalyzed synthesis route, longer curing of the gel in acidic media results in aerogels that have higher densities compared to those that have had shorter curing time.

For comparison, the theoretical densities were calculated as the ratio of the polymer mass to the volume of the gel, adapting the formula suggested for inorganic aerogels [100] for two extreme cases (Eq. 2): in the first case FA is assumed to form the maximum density of methylene bridges ($\rho_{th, -C-}$) and in the second case, the maximum density of dimethylene ether bridges ($\rho_{th, -C-O-C-}$) at specific 5MR/FA and W/5MR molar ratios is being assumed.

$$\rho_{th} = \frac{m_{polymer}}{V_{gel}} = \frac{m_{5MR} + x \cdot m_{FA} - m_{H_2O,c}}{\left(m_{H_2O} + (1-x) \cdot m_{FA} + m_{H_2O,c}\right) / \rho_{H_2O}} \qquad (2)$$

The polymer is formed from 5MR (m_{5MR}-mass of 5MR, g) and FA (m_{FA}-mass of $100 \cdot x$ % FA solution). The mass of the polymer is lower than the summed masses of the monomers by the mass of released water molecules during polycondensation ($m_{H2O,c}$- mass of the polycondensed water which depends on the linkages formed between 5MR molecules during polycondensation).

V_{gel} is the total volume of the gel. As a rough approximation, V_{gel} was considered equal to the volume of water from the solvent (m_{H2O}), FA solution, and the polycondensation of the monomers. ρ_{H2O} is the density of water.

Next to the two extremes of theoretical densities, the real densities of 5MR-FA aerogels, prepared using base-acid double catalyzed synthesis route, are plotted on Figure 3-2.

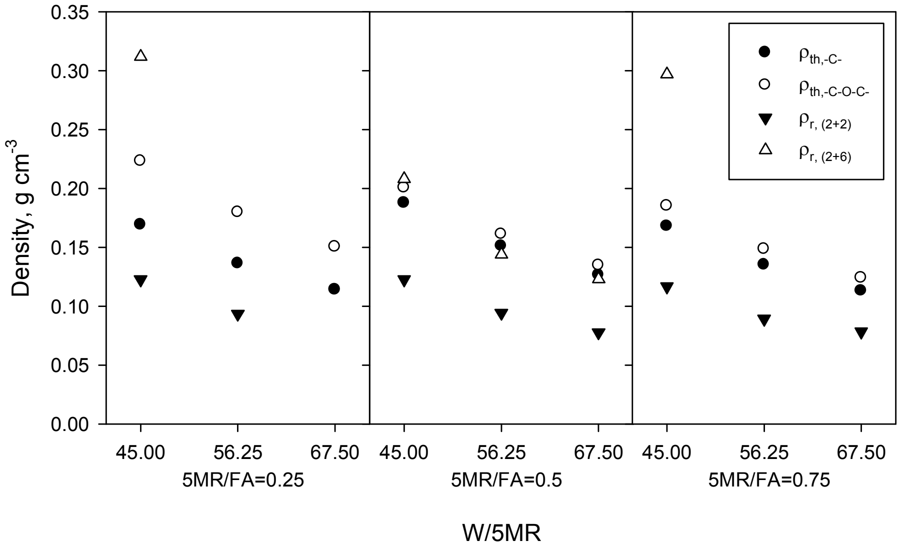


Figure 3-2 Densities of 5MR-FA aerogels (5MR/C=60) depending on 5MR/FA and W/5MR molar ratios. Theoretical densities $\rho_{th,-C-}$ and $\rho_{th,-C-O-C-}$ correspond to maximum formation of methylene or dimethylene ether bridges, respectively. Real density $\rho_{r,\,(2+2)}$- double-catalyzed synthesis comprises curing 2 days at base conditions and 2 days at acidic media. Real density $\rho_{r,\,(2+6)}$- double-catalyzed synthesis comprises curing 2 days at base conditions and 6 days at acidic media.

Short time curing in acidic media ($\rho_{r,\,(2+2)}$) results in aerogels with noticeably lower densities compared to the trend based on theoretical calculations. In the 5MR/FA range of 0.25-0.75 the densities are not greatly influenced by the 5MR/FA molar ratio. A longer curing period in acidic solution (6 days) results in higher aerogel densities compared to aerogels that were cured 2 days in acidic media. The densities are more dependent on the W/5MR ratio than on 5MR/FA ratio, and the densities closest to the calculated results are achieved at 5MR/FA=0.5. For analyzing the effect of acidic media on the extent of the cross-linking in the gel, the IR spectra of base, acid and base-acid catalyzed aerogels were measured and compared (Figure 3-3).

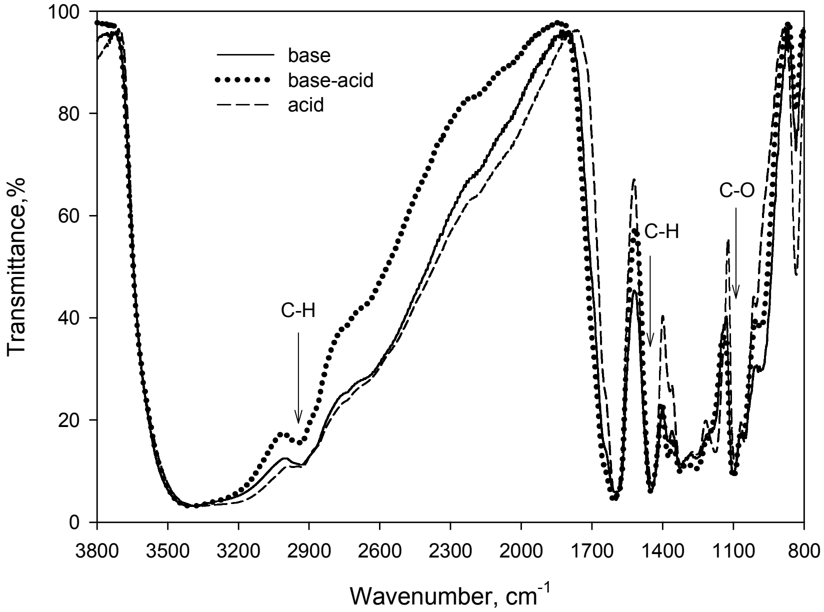


Figure 3-3 IR spectra of base, base-acid and acid catalyzed 5MR-FA organic aerogels (5MR/FA=0.5, 5MR/C=60, W/5MR=45)

In the spectra the IR absorption bands at 2930 cm^{-1} and 1450 cm^{-1} correspond to $-CH_2-$ linkages and have rather similar absorbancies for both, base and base-acid double-catalyzed aerogels. At 1100 cm^{-1} the absorptions are similar as well, however, in this region, the absorption may be caused by both, C-O bending vibrations of formaldehyde condensation products such as polymethylene glycol, hemiformal etc., and $-CH_2-O-CH_2-$ linkage between aromatic rings. Based on IR spectra, a firm conclusion about which linkages between aromatic compounds are preferred cannot be drawn. The noticeable difference between the relative intensities of the absorption can be found at 840 cm^{-1} where the absorbance of acid-catalyzed 5MR-FA aerogel shows the highest absorption at the frequency characteristic of substituted aromatic rings, referring to a higher degree of cross-linking between aromatic rings. The sol-gel reaction performed solely at acidic conditions, however, did not lead to homogeneous low density material at chosen molar ratios.

In order to determine whether the double-step base-acid catalyzed gel synthesis gives rise to better structural performance, the shrinkage occurring during supercritical drying was calculated (Eq. 1) and the results are shown on Figure 3-4. In the figure the effect of W/5MR on shrinkage of the material during the drying step can also be seen. At higher W/5MR ratio (the polymer concentration is lower) the shrinkage is higher as well. This result is in accordance with the shrinkage data of cresol based aerogels [48] where this is attributed to the solid gel network being sparsely packed at low polymer concentration, and therefore surviving the drying with higher shrinkage.

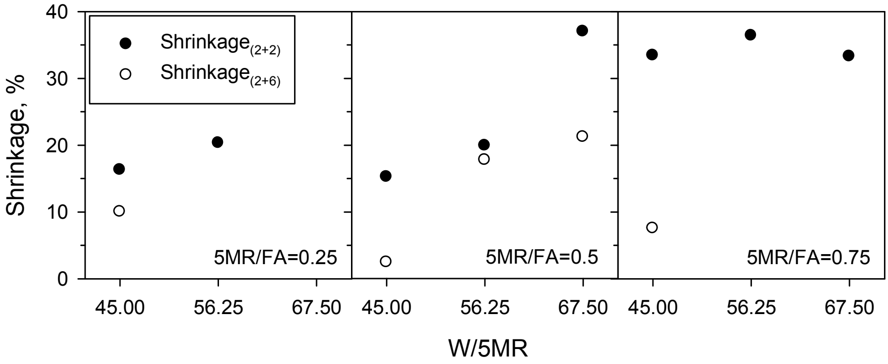


Figure 3-4 Shrinkage upon drying depending on molar ratios 5MR/FA and W/5MR

The gel shrinkage during drying is higher at shorter curing time ((2+2)- curing 2 days in basic and 2 days in acidic media) from which it can be deduced that the structure of the gel is less thoroughly developed by the time of the drying step, compared with gels cured in acid medium for a longer time (2+6). A lower 5MR/FA ratio (higher FA amount) results in gels with higher structural stability.

The comparison of IR absorption spectra of 5MR-FA aerogels with 5MR/FA ratios 0.25, 0.5 and 0.75 show that at higher FA concentration the absorption at 2950 cm^{-1} is increased, referring to increased content of $-CH_2-$ in the polymer structure (Figure 3-5). At higher FA concentration, the absorption of C-O stretching at 1100 cm^{-1} is also increased. At 840 cm^{-1} the band can be recognized which describes the content of substituted aromatic rings with the absorption decreasing in the following order of 5MR/FA ratio: 0.75>0.5>0.25, which is in correlation with the percentage of 5MR in the solution. Yet again, the difference between the spectra is rather small.

The effect of curing the gel in acidic media was recognized as a tool for neutralizing the base catalyst in order to avoid sodium carbonate, being insoluble in acetone, from precipitation during the solvent exchange.

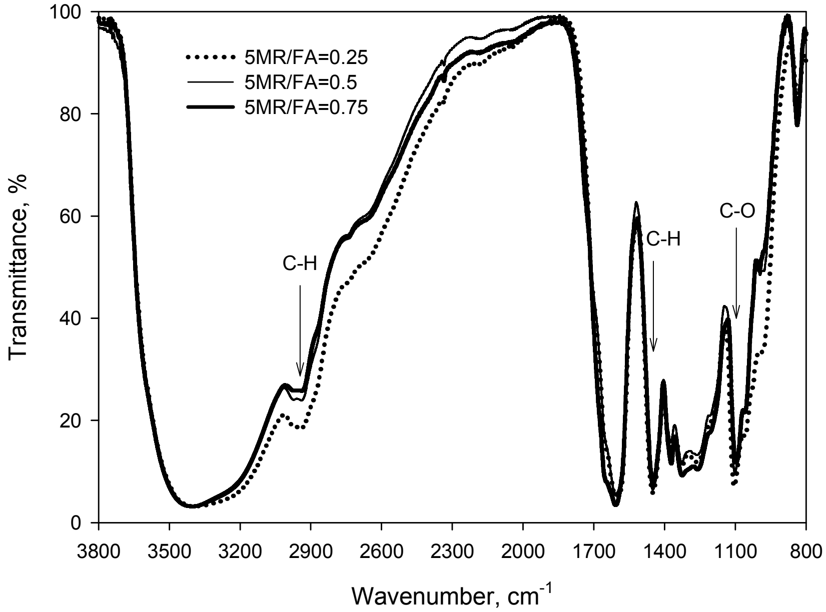


Figure 3-5 IR absorption of aerogels prepared at 5MR/FA molar ratios 0.5, 0.25 and 0.75

3.1.2 Morphology

Upon varying the 5MR/FA ratio, a considerable effect on the particle size was not achieved (Figure 3-6).

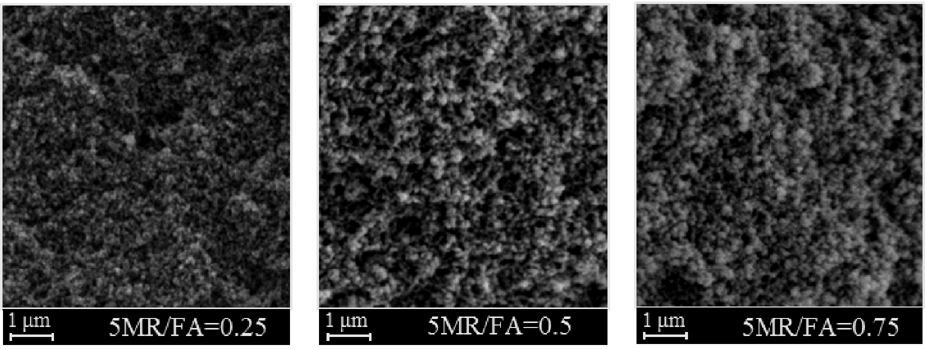


Figure 3-6 SEM micrographs of the structure of 5MR-FA organic aerogels at 5MR/FA molar ratios 0.25, 0.5 and 0.75 (5MR/C=60, W/5MR=45)

The effect of catalyst concentration on aerogel morphology can be followed on SEM micrographs presented on Figure 3-7 and it is in accordance with the model shown in Figure 1-7. In the case of 5MR/C=16 (Figure 3-7a) the particles with diameter approximately 10 nm were obtained, an aerogel prepared at 5MR/C=60 (Figure 3-7b) resulted in material composed of particles with a size around 20 nm.

Supercritical drying is a necessary step in order to obtain low density 5MR-FA aerogels. Comparing 5MR-FA gel samples dried via SFE and via conventional evaporation (Figure 3-7) it can be seen that in the case of evaporation at ambient conditions, the porosity of the material is significantly reduced. This is reflected also by increased density and shrinkage (Table 3-1).

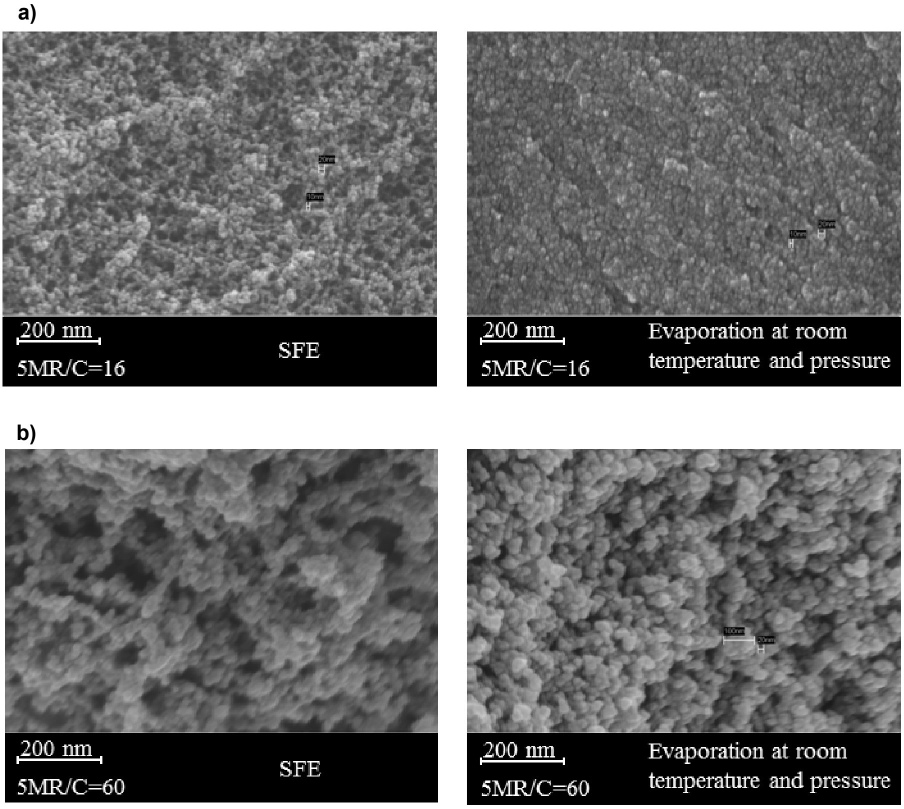


Figure 3-7 The influence of preparation conditions on the morphology of the material: a) 5MR/FA=0.5, 5MR/C=16, W/5MR=45; b) 5MR/FA=0.5, 5MR/C=60, W/5MR=56.25 dried via supercritical fluid extraction (SFE) or conventional evaporation at room temperature and pressure

The specific surface area of the gel 5MR/C=60 was not affected by the duration of dynamic extraction of gel with liquid CO_2 within tested drying regimes. At the catalyst ratio 5MR/C=16, the density of the material was significantly higher and acetone was not thoroughly removed from the gel pores using the extraction regimes that were suitable for drying the gels with 5MR/C=60. This may be a sign of the polymeric nature of the gel as opposed to the colloidal. Longer drying time did allow lowering the shrinkage and density of the gels. As can be recognized on Figure 3-7, the drying method does not have an intensive influence on the size of the gel particle. The gels prepared under molar ratios 5MR/FA=0.5, 5MR/C=16 and W/5MR=45, and dried via SFE or conventional evaporation, reveal 10 nm particles having rather uniform particle size distribution in both cases. The situation is similar for gels with molar ratios 5MR/FA=0.5, 5MR/C=60, W/5MR=56.25, consisting of particles in the same range in both cases of drying.

Table 3-1 The effect of the catalyst amount and the drying time on the density and shrinkage of aerogels. 5MR/F = 0.5, W/5MR = 45

5MR/C	**CO_2 drying regime*, h**			**SFE**			**Evaporation**		
	200 bar, 25°C	100 bar, 25°C	100 bar, 50°C	Density, g cm^{-3}	Shrinkage, %	S_{BET}, m^2 g^{-1}	Density, g cm^{-3}	Shrinkage, %	S_{BET}, m^2 g^{-1}
60	0.33	2.5	2	0.21	2	323	0.46	56	294
	0.33	2	2	0.21	4	351	0.46	47	294
	0.33	1.5	2	0.21	8	318	0.46	59	294
	0.33	1	2	0.21	6	328	0.46	56	294
16	0.33	2	6	0.58	46		1.35	69	
	0.33	2.5	2	0.92	61		1.35	69	

*10 mL high-pressure cell

The gels obtained at 5MR/C=60 were beige and opaque in color, the gels with higher catalyst concentration (5MR/C=16), consisting of smaller particles, were transparent. Drying either way did not maintain the transparency of the gel. Although it was found that the specific surface areas of conventionally dried gels, compared to the gels dried using SFE, was only slightly lower, the cracking, high density and apparent decrease in porosity occurred, which can be avoided with supercritical drying. In order to obtain a high quality of drying, it is necessary to use the optimized regime of supercritical extraction that considers the parameters of the reactor and the specific sample.

In the experiments carried out by the author, 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 shrinkage was observed. The specific surface area was also measured. At optimal molar ratios, a drying shorter than 4.5 h resulted in the 5MR-FA aerogel with a shrinkage of 4%, density of 0.21 g cm^{-3} and specific surface area of 350 m^2 g^{-1}.

3.2 Honeyol™-formaldehyde aerogels

3.2.1 Gel formation

A study was conducted in order to obtain a gel from technical mixture of dihydroxybenzenes available at an oil shale processing industry. Unlike 5MR, Honeyol™, containing multiple substituted dihydroxybenzenes, did not lead to gel formation in an aqueous solvent in the presence of Na_2CO_3 at room temperature. The gel, however, formed when the amount of catalyst and the gelation temperature were increased. The double-step base-acid catalyzed gel monolith dissolved in acetone during the solvent exchange. Although methanol was found to be a satisfying alternative for solvent replacement, methanol was chosen as the original solvent following the examples from the literature [81] to eliminate the need for the solvent exchange entirely, in order to be able to shorten the aerogel preparation process. KOH was used as the base catalyst, because Na_2CO_3 is poorly soluble in alcohol.

The gel time of Honeyol™ based sols is much longer compared to 5MR-FA gels. As shown on Figure 3-8 the increase in H/C ratio (lower catalyst concentrations) results in increasingly longer gel time.

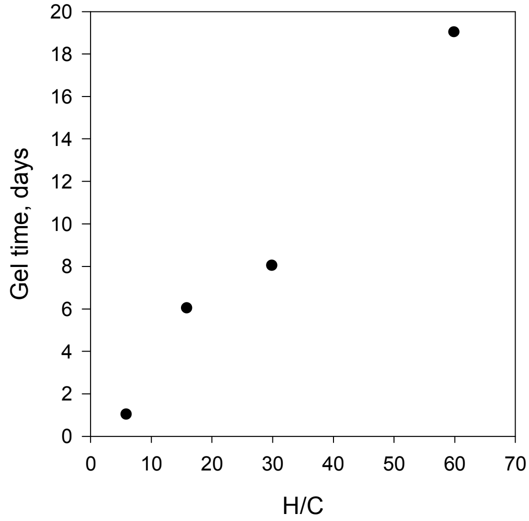


Figure 3-8 Gel time for H-FA sols at 60°C (H/FA=0.5, methanol/H=45)

The sol prepared using the molar ratios H/FA=0.5, methanol/H=45 and H/C=60 turns into gel after curing it 19 days at 60°C. The gel time can be reduced by decreasing the catalyst ratio: at H/C ratio 6 the gel forms within 1 day. Despite long gel times at low catalyst concentrations, the gels obtained were homogeneous: the sols were stable and no precipitation occurred.

The effect of the acid catalyst in the double-step base-acid catalyzed H-FA aerogel, similarly to 5MR-FA, could not be confirmed with IR measurements.

By excluding the step of catalyzation in acidic media, the aerogel preparation time could be shortened by several days.

On Figure 3-9 the absorption bands corresponding to methylene and dimethylene ether bridges between the aromatic monomers in SFE dried R-FA, 5MR-FA and H-FA aerogels can be compared. Aerogels based on di- and tri-substituted aromatic precursors show similar C-O absorption at 1100 cm^{-1}. Methylene bridges at their characteristic wavenumbers (2930 cm^{-1} and 1450 cm^{-1}) show stronger absorption for R-FA aerogel than for 5MR-FA and H-FA aerogels.

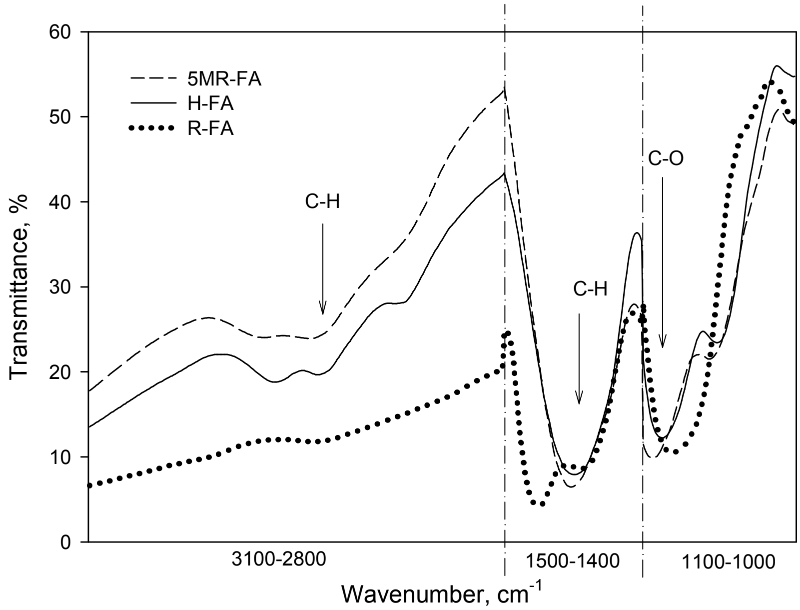


Figure 3-9 IR absorption of methylene and dimethylene ether bridges in R-FA, 5MR-FA and H-FA aerogels

3.2.2 Morphology

The morphology of H-FA aerogels is similar to 5MR-FA aerogels tunable by varying the concentrations of reagents in the sol, and is most effective via the catalyst concentration. On Figure 3-10 the structural parameters of the gels prepared either by single-step base catalyzed or double-step base-acid catalyzed synthesis can be compared. At single-step catalyzed synthesis, the density of aerogel monoliths is lower and porosity and specific surface area are slightly higher. At H/C=60 S_{BET} and V_{tot} for base catalyzed aerogel are 355 m^2 g^{-1} and 624 mm^3 g^{-1}, respectively. The corresponding characteristics for base-acid catalyzed aerogels are 302 m^2 g^{-1} and 581 mm^3 g^{-1}. Increasingly lower H/C ratio gives an increasingly larger specific surface area and higher porosity in the studied H/C range.

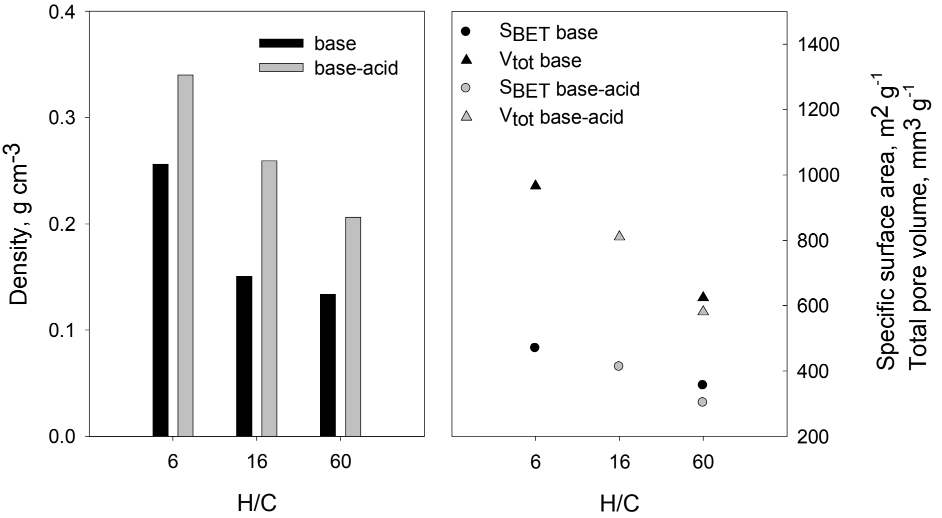


Figure 3-10 The influence of the catalysis on the density, the specific surface area (S_{BET}) and on the total pore volume (V_{tot}) of H-FA aerogels (methanol/H=45, H/FA=0.5)

On Figure 3-11 the SEM micrographs show that H-FA aerogels with H/C ratios 60 and 6 follow the same trend as R-FA [35,57,94] and 5MR-FA aerogels: a higher catalyst concentration leads to formation of smaller colloidal particles and the aerogel particles visible on SEM images are smaller, and the pores are smaller which is commensurate with the results of surface area and porosity dependence on H/C ratio.

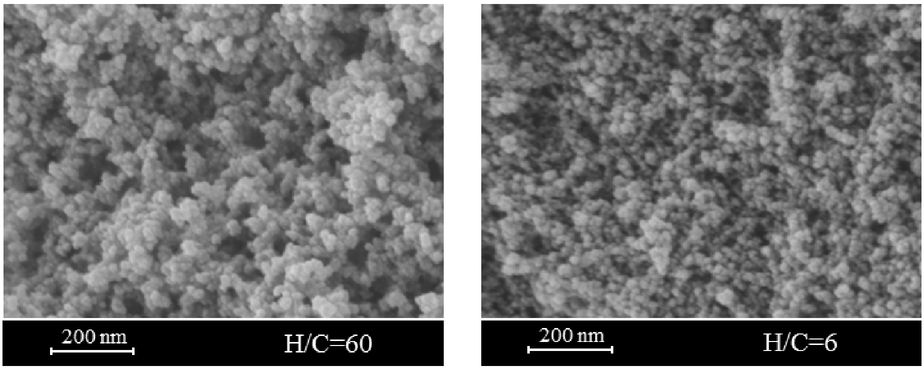


Figure 3-11 Effect of the catalyst concentration on supercritically dried H-FA aerogels:SEM images of H-FA aerogels with H/C ratios=60 and 6 (methanol/H=45, H/FA=0.5, double-step base acid catalyzed synthesis)

H/C ratio 6 leads to transparent gels with a particle size of 10 nm; the gels with the H/C ratio 60 are opaque and have more than 20 nm sized particles. Pore size distribution for unpyrolyzed organic aerogels is wide and no micropores were detected with nitrogen sorption measurements.

3.2.3 Density and shrinkage

The shrinkage (Eq. 1) at single- and double-catalyzed aerogels seemed, surprisingly, not to depend on H/C molar ratios (H/C=6, 16 and 60). Compared to 5MR-FA gels, the shrinkage of H-FA gels was huge, losing roughly 35-55% of its cross-sectional area during drying. Based on these results, the increase in density can be said to happen during aging in acidic media, and is not due to the poor durability of the structure during supercritical drying. It is known that in methanol the presence of an acid catalyst leads unreacted formaldehyde to the formation of hemiformal [88], hindering further cross-linking between the molecules, which may also contribute to the huge shrinkage of H-FA gel while processing.

The density of H-FA aerogels was found to be affected by the drying time. As aerogel preparation from Honeyol™ does not include the solvent exchange step, but during the gel formation through the polycondensation some water is generated, the drying process should last long enough to remove all the water from the pores. Yet, with 5h and 35min supercritical drying, the lowest density for H-FA aerogel prepared using the single-step base catalyzed synthesis was 0.10 g cm^{-3}.

If, in the case of 5MR-FA drying at room temperature and pressure resulted in higher density (0.46 g cm^{-3}) and decreased specific surface area (294 m^{2} g^{-1}), then in the case of H-FA gels, the gel rod cracked into pieces due to the capillary pressure, thus showing the importance of the supercritical fluid drying in the aerogel preparation process.

In the case of using an industrial raw material, it should be taken into account that its chemical composition may vary and it can affect the correlations between the concentrations and the structural properties.

3.3 5-methylresorcinol- 2,6-dihydroxy-4methyl benzoic acid-formaldehyde aerogels

An organic alternative to the inorganic catalyst was desired, in order to be able to prepare aerogels without inorganic additives. Benzoic acid and alternative hydroxy derivatives of benzoic acid, such as 4-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid and 2,6-dihydroxy-4-methyl benzoic acid (dHMBA) were tested as potential catalysts for gel preparation. A homogeneous gel was obtained when dHMBA or 2,6-dihydroxybenzoic acid was used, but the focus was set on the use of dHMBA because it led to substantially faster gelation when compared to 2,6-dihydroxybenzoic acid.

3.3.1 Gel formation

dHMBA has a sufficient acidity to promote the polymerization of the monomers. As its molecular structure is similar to the monomer, 5MR, it was expected that that derivative of benzoic acid would also get incorporated in the aerogel backbone. The function of dHMBA as a monomer was tested by preparing a sol from dHMBA with FA in ACN without 5MR in the mixture. A transparent yellow sol turned opaque in 1 h, but a solid gel did not form. On Figure 3-12 the IR spectra of dHMBA-FA polymer and the raw monomer dHMBA can be compared. The spectrum of dHMBA-FA shows the absorptions characteristic to methylene and dimethylene ether bridges similar to 5MR-FA gel (see Figure 3-3). In addition, the absorption bands at 1680 cm^{-1} and 1200 cm^{-1} indicate the C=O and C-O bonds from carboxyl group of dHMBA.

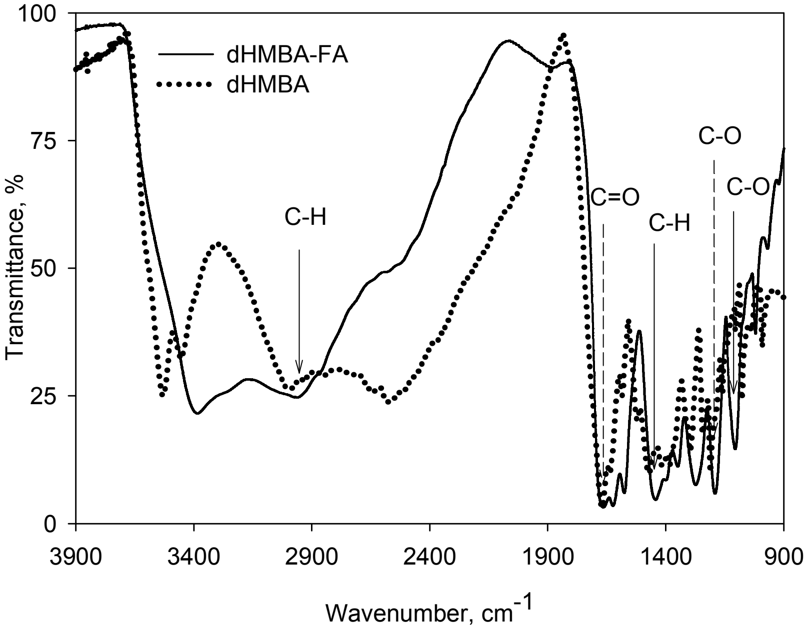


Figure 3-12 IR spectra of dHMBA-FA polymer and raw dHMBA

Based on IR spectra, it is not clear whether the polymerization occurs also via carboxyl group because the absorption bands of C-O and C=O from carboxyl and ester groups absorb IR at close frequencies. Therefore, the evolution of gel formation was monitored using NMR spectroscopy to confirm the bifunctionality of dHMBA- a sample with a %5MR/%dHMBA molar ratio 50/50 was used. On the ^{13}C NMR spectra (Figure 3-13), the new signals of esters were expected to appear in the area of lower frequency, than a signal of carboxylic carbon in parent acid (<172 ppm). On the enlargement of the spectral fragment recorded after 35 minutes (Figure 3-13b) it can be seen that the only new signals corresponding to the carboxylic carbons were resonating at higher frequency (173 ppm) than its parent acid. These signals can be attributed to newly formed carboxylic acids, which are intermediates of polymerization, and the ester formation was not observed. Faster consumption of 5MR than dHMBA can be followed on NMR spectra, which is due to the deactivating influence of carboxyl group of dHMBA in aromatic substitution.

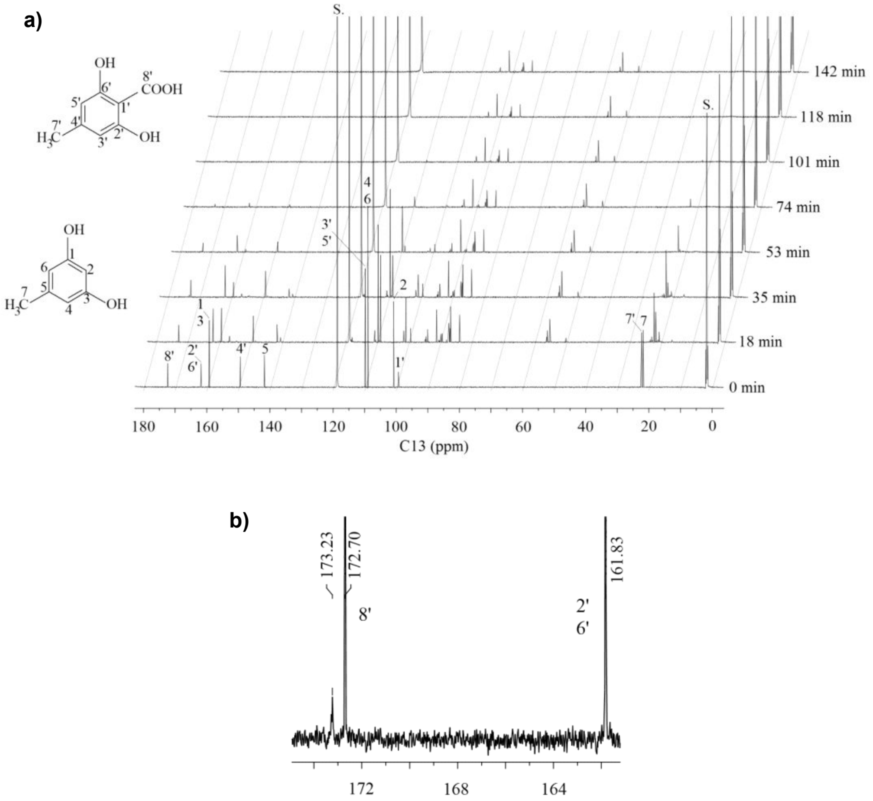


Figure 3-13 a) ^{13}C NMR spectra of 5MR-dHMBA-FA sol in CD_3CN recorded during142 minutes after the addition of FA, b) enlargement of the spectra recorded 35 minutes after the addition of FA

NMR spectra also give information on gel time. The spectra indicated as 0 min were measured before adding FA solution to the sample, and the subsequent spectra were recorded during the 142 minutes following the addition of FA. The formation of new compounds can be seen after the addition of FA, and the disappearance of all aromatic signals within 2 hours, only intermediates of the sol formation in solution phase could be recorded. The new signals on the spectra between 83-95 and 50-57 ppm are from FA solution and can be attributed to condensation products of FA and methanol.

Figure 3-14 depicts the effect of the %5MR/%dHMBA ratio on the gel time. The correlation between the ratio of 5MR to dHMBA and the morphology of the resulting aerogel is complicated due to the dual role of dHMBA in the system (a comonomer and a reaction promoting agent). In the case of 5MR and H, similar to resorcinol, the gel time on decreasing monomer to catalyst ratio was gradually decreasing. The results were quite different for 5MR-dHMBA-FA gels when varying the ratio %5MR/%dHMBA.

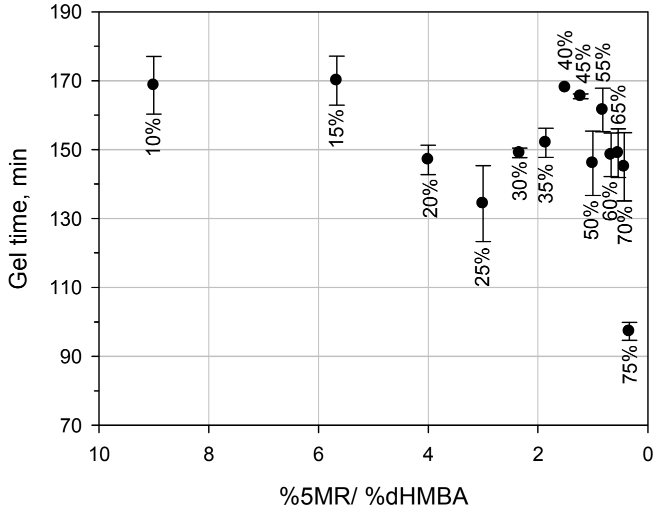


Figure 3-14 Gel time at different %5MR/%dHMBA ratios at 25°C (the exact value of %dHMBA is depicted next to each data point)

At lower dHMBA concentrations (10-25%) the speed of polycondensation increased as the amount of benzoic acid derivative (dHMBA) was increased. At the same time, the increased amount of comonomer (dHMBA) with two available reaction sites slows the formation of a solid cross-linked network. This effect could be noticed when the amount of dHMBA was increased from 25 to 40%. From 40% of dHMBA the rate of gelation again increased which may be related to the formation of a different type of polymer structure.

3.3.2 Morphology

On SEM micrographs (Figure 3-15), it can be seen that the morphology of the materials at ratios 75/25 and 25/75 are completely different. When the amount of 5MR prevails, the structure of the aerogel is composed of uniform spherical particles (diameters 24-25 nm), which is similar to that of 5MR-FA and H-FA aerogels. Increasing the percentage of dHMBA leads to the presence of large macropores (pores with diameter > 50 nm), due to the formation of strings of particles. Strings of particles with a broad size distribution can already be observed at a %5MR/%dHMBA ratio 60/40 which correlates well with the results of gel time measurements. At 25/75, the particle size distribution is again quite uniform, with diameters of approximately 15 nm. The morphology of aerogels 50/50 and 25/75 appears to be similar. The strings of particles are longer at higher dHMBA concentration, and the macropores are larger. Although the yellow color of the sols intensified when the percentage of dHMBA was increased, all the gels in the examined range were transparent and equally bright orange in color. After drying, the transparency remained to some extent, while aerogels with a higher percentage of 5MR were darker than those with a higher percentage of dHMBA, the color ranging from dark red to bright orange, respectively.

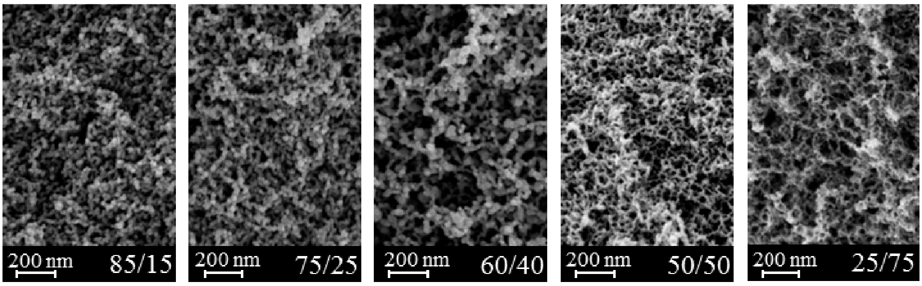


Figure 3-15 SEM micrographs of aerogels prepared at different %5MR/%dHMBA ratios

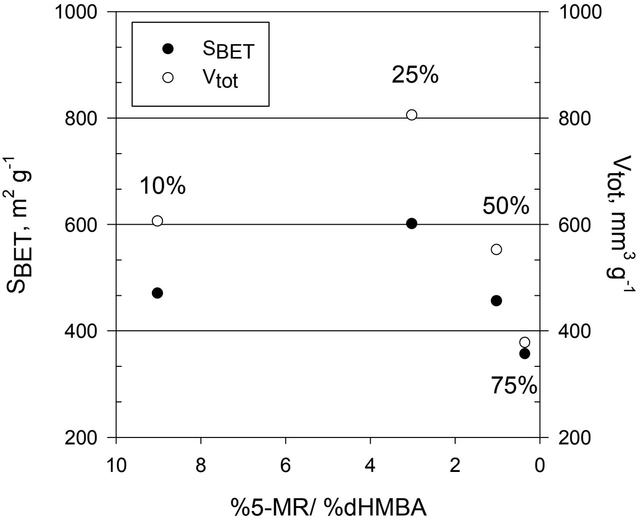


Figure 3-16 Specific surface area (S_{BET}) and total volume of pores (V_{tot}) of aerogels with different ratios of %5MR/%dHMBA (the exact value of %dHMBA is depicted next to the data point)

Measurements of nitrogen sorption showed that an increase in the amount of acidic comonomer increases the specific surface area of the material, and the total volume of the pores in the limited range of the dHMBA concentration. The highest specific surface area and the largest total pore volume, 600 m^2 g^{-1} and 800 mm^3 g^{-1}, respectively, were achieved at %5MR/%dHMBA ratio of 75/25, as is clearly demonstrated in Figure 3-16. Compared to 5MR-FA and H-FA aerogels, these values for 5MR-dHMBA-FA aerogel are considerably higher. There were no micropores in 5MR-dHMBA-FA organic aerogels.

3.3.3 Density and shrinkage

Unlike 5MR-FA and H-FA aerogels, decreasing %5MR/%dHMBA ratio for 5MR-dHMBA-FA aerogels, material with a lower density is achieved (Figure 3-17) which based on SEM results, is related to formation of increasingly large macropores in the gel. Increasing macroporosity facilitates easy removal of the solvent from the gel leading to smaller shrinkage of the material during drying. However, from %5MR/%dHMBA ratio of 30/70 the density and shrinkage started to increase, which is most likely due to an increasingly tenuous network, which is not supporting the overall shape of the monolith sufficiently. Aerogels become brittle. Along with the volume decrease during drying, the density of the aerogel increases.

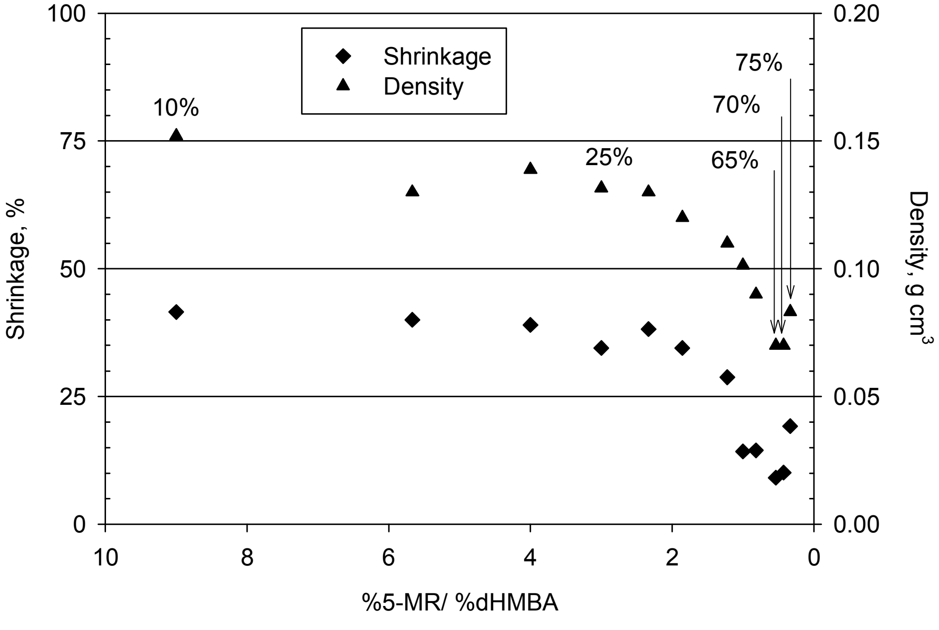


Figure 3-17 Shrinkage during SFE drying and the densities of aerogels at different %5MR/%dHMBA ratios

3.4 Thermogravimetric characterization of the products

Organic aerogels are mainly used as the source for carbon aerogels, and TGA is a good method for characterizing the process of carbonization, and looking for differences in the case of different precursors. As the carbonization of the organic aerogel is in most cases carried out via high temperature treatment under nitrogen flow, the analysis was performed in N_2 atmosphere. The TGA curves of 5MR-FA, H-FA and 5MR-dHMBA-FA on Figure 3-18a show that 5MR-FA aerogel has less burn-off compared to H-FA and 5MR-dHMBA-FA aerogels. In Figure 3-18b, it can be seen that the increased concentration of dHMBA results in higher mass loss during carbonization. Next to overall mass loss is the calculated mass of oxygen atoms of carboxyl groups originating from dHMBA, and the trends of those two mass losses are the same.

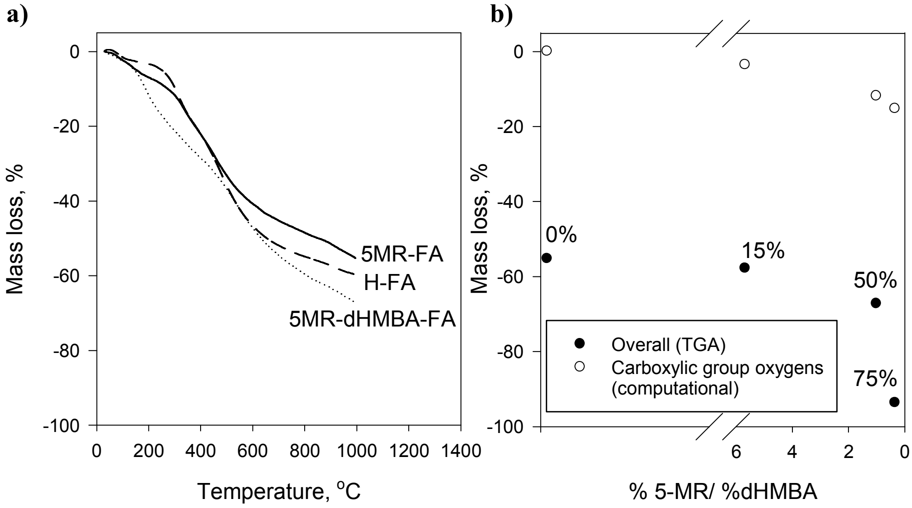


Figure 3-18 Mass loss of (a) 5MR-FA, H-FA and 5MR-dHMBA-FA (%5MR/%dHMBA is 50/50) aerogels and (b) 5MR-dHMBA-FA aerogels at different dHMBA concentrations during heat treatment at nitrogen atmosphere (performed on SETARAM LabSys 2000 TG/DTA equipment with N_2 (99.999%) flow of 50 ml min^{-1} at a heating rate 10°C min^{-1} in a Pt crucible)

4 CONCLUSIONS

The main goal of this thesis was to demonstrate that oil-shale origin raw material 5-methylresorcinol is a considerable alternative source for aerogel preparation and, as a result of this work, three separate routes for obtaining organic aerogels were successfully developed.

- As the morphology of the materials obtained can be finely tuned on a nanometrical level, the 5MR based organic aerogels are fine precursors for carbon aerogel preparation.
- The possibility to use a technical unpurified mixture of alkyl-substituted benzene-1,3-diols as an alternative raw material for aerogel production was presented. The technical mixture may not be the first choice for high technology applications but it can be a considerable alternative when talking about adsorbents or insulation materials.
- An organic aerogel based on 5-methylresorcinol and an organic acidic comonomer was a good example of the optimization of the production route towards fast aerogel production where the aerogels free of inorganic additives were obtained. In addition, the development and tunability of large macropores of the structure of that type of aerogels gives another character to the material, increasing the range of potential applications of 5-methylresorcinol based aerogels.

The oil-shale based precursors allow us to obtain aerogels with versatile morphology.

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ABSTRACT

Organic aerogels are known as precursors for carbon aerogels which are unique materials due to highly porous structure, high specific surface area and electrical conductivity. Over time new precursors, solvents, preparation methods etc. have been looked for in order to reduce the cost, time and energy of aerogel production. In the current thesis, an alternative raw material for aerogel preparation is used- 5-methylresorcinol. This precursor is of oil-shale origin and was obtained as the by-product of the local oil shale processing industry. In the current research both, purified 5-methylresorcinol and the technical mixture of alkyl-substituted 1,3-dihydroxybenzenes could successfully be used.

5MR-FA aerogels were prepared following a known four-step process comprised of gel preparation in aqueous media in the presence of inorganic base catalyst, curing in acidic media to further promote the reaction, solvent exchange and drying the gel via supercritical fluid extraction. As the result of the study, it was found that the process could be shortened by excluding the step of curing in acidic media. The method was developed further and H-FA gel was prepared in a different solvent that allowed eliminating the step of solvent exchange which would take several days and a high amount of extra solvent. The process was further developed with the aim to replace inorganic catalyst with an organic alternative and as a result an aerogel prepared using acidic comonomer dHMBA together with 5MR and FA.

The aerogel preparation routes developed allowed tuning the morphology of the material at nanoscale effectively by choosing suitable monomer and catalyst concentrations in the sol similarly to aerogels from phenolic aerogel precursors known from the literature. Aerogels based on 5MR allowed achieving densities around 0.10 g cm^{-3} and the specific surface areas over 350 m^2 g^{-1}, for 5MR-dHMBA-FA aerogel the specific surface area as high as 600 m^2 g^{-1}, could be obtained.

As the comonomer being incorporated in the aerogel structure is at the same moment responsible for promoting the reaction, the tuning of the morphology is somewhat complicated because the correlations between the structure and the concentration of the reactives is not straightforward, however this sort of combinations allows to extend the assortment of structures that can be obtained based on 5MR. The materials with very low densities could be achieved and the structure with uniform particles packed sparsely with high level of macroporosity.

The materials obtained were studied using IR spectrometry, SEM, nitrogen sorption analysis and the gel formation chemistry in the case of using an acidic copolymer was monitored using NMR spectroscopy. In order to predict the changes of the organic aerogel during the carbonization which would be the following step, the thermogravimetric analysis was also carried out.

KOKKUVÕTE

Orgaanilised aerogeelid on väga poorsed väikese tiheduse ja suure eripinnaga materjalid, mida kasutatakse enamjaolt süsinikaerogeelide valmistamiseks. Süsinikaerogeelide struktuur on sarnane orgaanilise aerogeeli struktuuriga, lisaks omab materjal elektrijuhtivust ja on seetõttu väärtuslik materjal elektroonilisteks rakendusteks. Orgaaniliste aerogeelide valmistamiseks otsitakse pidevalt võimalusi valmistamisprotsessi kulude vähendamiseks. Käesolevas doktoritöös on demonstreeritud aerogeeli valmistamiseks 5-metüülresortsinooli- lähteainet, mis on pärit kohalikust põlevkivitööstusest ja on põlevkivi töötlemise kõrvalsaadus. Töö käigus töötati välja sobilik metoodika aerogeeli saamiseks puhtast 5-metüülresortsinoolist ja ka tehnilisest segust Honeyol™, milles on 5-metüülresortsinooli sisaldus veidi alla 60%.

5MR-FA aerogeelide valmistamiseks kohaldati kirjandusest tuntud metoodikat, mis koosnes neljast etapist: geeli valmistamine anorgaanilse aluskatalüsaatori juuresolekul vesikeskkonnas, geeli hoidmine happelises keskkonnas geelivõrgustiku tihedamaks muutmiseks, solvendivahetusetapp ja geelist solvendi eemaldamine ülekriitilises olekus süsinikdioksiidiga. Uurimise tulemusena leiti, et protsessi võib lühemaks muuta geeli happelises keskkonnas töötlemise etapi võrra. Metoodikat arendati edasi ja H-FA geel valmistati solvendis, mis lubas välja jätta solvendivahetusetapi, millele kuluks mitu päeva ja suur kogus solventi. Järgmine arendus kätkes anorgaanilise katalüsaatori asendamist orgaanilisega, et lõpp-produk oleks vaba anorgaanilistest komponentidest: 5MR-FA geel valmistati kasutades happelist komonomeeri dHMBA.

Metoodikad, mis 5-metüülresortsinooli baasil aeogeelide saamiseks välja arendati, võimaldavad materjali nanostruktuuri, sarnaselt teistele fenoolsetele aerogeeli lähteühenditele, mõjutada. Tõhus viis soovitud eripinna, poorsuse või tiheduse saamiseks on valida sobivad monomeeride ja katalüsaatori kontsentratsioonid. 5-metüülresortsinooli baasil saadavate aerogeelide tihedus küündis nii madalale kui 0,10 g cm^{-3}, 5MR-dHMBA-FA aerogeelil tiheduseni 0,07 g cm^{-3}. Eripinnad 5MR-FA ja H-FA aerogeelidel olid üle 350 m^{2} g^{-1}, 5MR-dHMBA-FA aerogeelil mõõdeti suurimaks eripinnaks 600 m^{2} g^{-1}.

Happelise komonomeeri kasutamine reaktsioonis muudab aerogeeli struktuuri mõjutamise komplitseeritumaks, sest komonomeer osaleb reaktsioonis samal ajal kui „katalüsaator“ ja monomeer. Vaatamata sellele võimaldab just selline kombinatsioon saada 5MR-FA ja H-FA ja R-FA aerogeelidest erineva struktuuriga materjale- geeli struktuur on väga hõre, selles on rohkelt makropoore ning saadava aerogeeli tihedus on oluliselt madalam.

Materjalide iseloomustamiseks kasutati infrapunaspektromeetriat, skaneerivat elektronmikroskoopiat, lämmastiku adsorptsioon/desorptsioon analüüsi ja happelise komonomeeri puhul uuriti geeli moodustumise käiku tuumamagnetresonants spektroskoopia abil. Iseloomustamaks orgaanilise aerogeeliga toimuvaid muutusi kõrgel temperatuuril, mille juures toimub süsinikaerogeeli valmistamine, viidi läbi ka termogravimeetriline analüüs.

ORIGINAL PUBLICATIONS

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Preparation of carbon aerogels from 5-methylresorcinol–formaldehyde gels

F. Pérez-Caballero [a,*], A.-L. Peikolainen [a], M. Uibu [b], R. Kuusik [b], O. Volobujeva [c], M. Koel [a]

[a] *Institute of Chemistry, Tallinn University of Technology, Akadeemia Tee 15, Tallinn 12618, Estonia*
[b] *Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate Tee 5, Tallinn 19086, Estonia*
[c] *Department of Materials Science, Tallinn University of Technology, Ehitajate Tee 5, Tallinn 19086, Estonia*

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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.

Keywords: Supercritical drying; Nitrogen adsorption; Supercritical carbon dioxide; Organic aerogel; Carbon aerogel; Porosity

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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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[*] Corresponding author. Tel./fax: +372 6204325.
E-mail address: fernanlora@hotmail.com (F. Pérez-Caballero).

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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-methylresorcinol (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 $\approx$ 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:

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

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} (m^2/g)	$S_{non\text{-}mic}$ (m^2/g)	S_{mic} (m^2/g)	V_{mic} (mm^3/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} (m^2/g) is the BET surface of the carbon aerogel. $S_{non\text{-}mic}$ (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 and finally, V_{mic} (mm^3/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, $\%S_{\text{mic}}$, the following equation was used:

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

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).

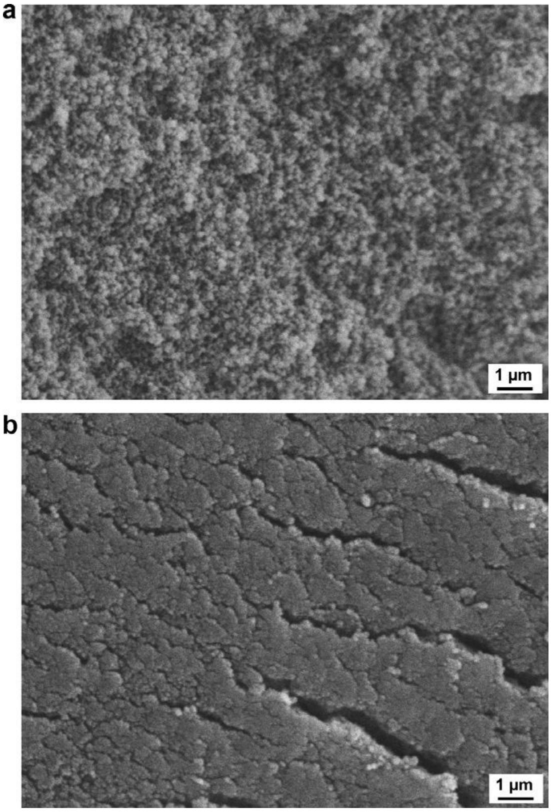

Fig. 1. (a) View of aerogel dried under supercritical conditions. (b) View of aerogel dried at ambient pressure and temperature.

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].

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

MR/ C	W/ MR	Density SCE (g/cm^3)	Density 973 K (g/cm^3)	Density 1273 K (g/cm^3)	$\Delta\Phi_{\text{SCE}}$ (%)
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, $\Delta\Phi_{\text{SCE}}$ refers to the linear shrinkage of the gel after drying it.

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/cm^3). 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.

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.

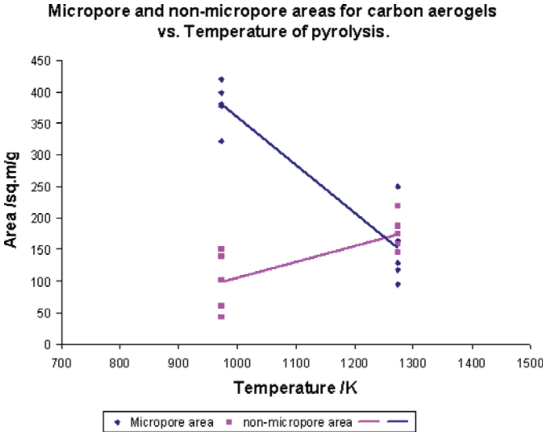

Fig. 2. Microporous and non-microporous surface areas of carbons aerogels versus pyrolysis temperature.

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,

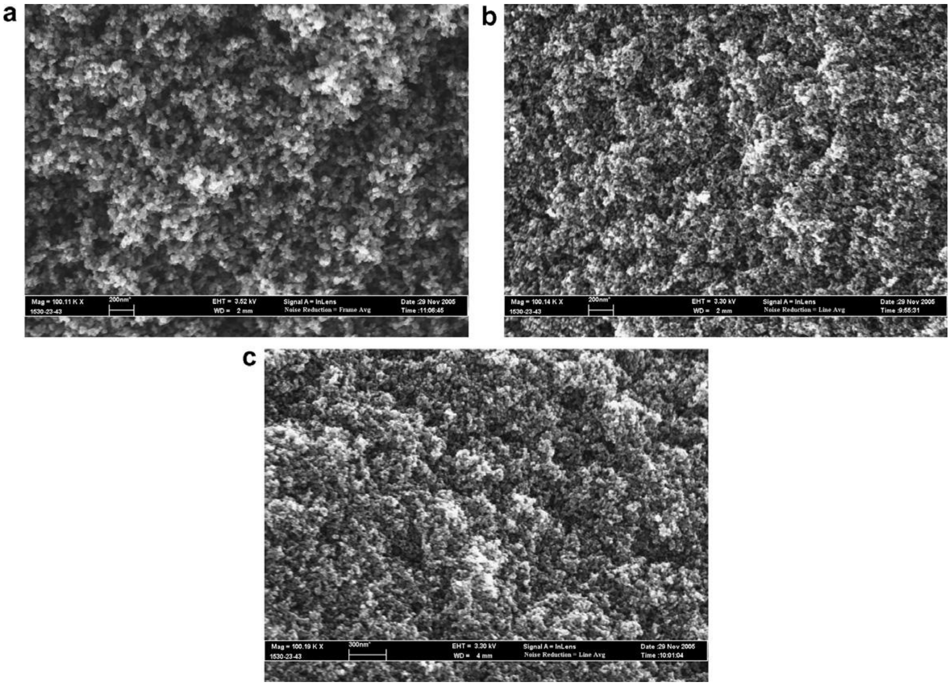

Fig. 3. (a) MR/C = 92, W/MR = 44 and MR/F = 0.5, 1273 K pyrolysis. (b) MR/C = 30, W/MR = 24 and MR/F = 0.5, pyrolysed at 1273 K. (c) MR/C = 30, W/MR = 24 and MR/F = 0.5, pyrolysed at 973 K.

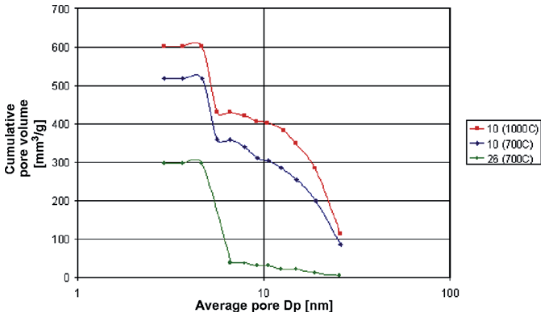

Fig. 4. The BJH pore size distribution of some samples.

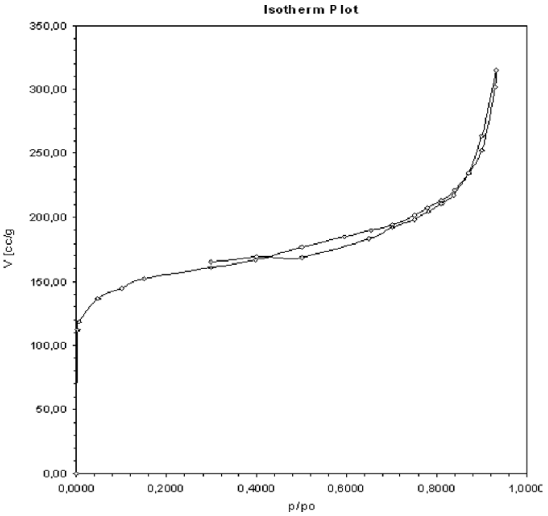

Fig. 5. The nitrogen adsorption isotherm of gel #12 (MR/F = 0.5, W/MR = 24 and MR/C = 90) pyrolysed at 973 K.

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-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 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

Peikolainen, A.-L., Pérez-Caballero, F., Koel, M. Orgaanilise aerogeeli valmistamise meetod (Method of preparation of organic aerogel gels) Patent EE200700032A (2007) from Tallinn University of Technology.

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(43) Patenditaotluse avaldamise kuupäev:	**16.02.2009**	(72) Leiutise autorid: **Anna-Liisa Peikolainen** **Rakvere tee 3-77, Kadrina,** **45201 Lääne-Viru maakond, EE** **Fernando Peréz-Caballero** **Suur-Patarei 7-18, 10415 Tallinn, EE** **Mihkel Koel** **Ehitajate tee 46-33, 12911 Tallinn, EE**

(54) Orgaanilise aerogeeli valmistamise meetod

(57) Väikese tihedusega orgaanilise aerogeeli valmistamise meetod, kasutades lähteainena formaldehüüdi ja 5-metüülresortsinooli tehnilist segu metanoolis. Geel kuivatatakse geelist ülekriitilises olekus fluidumi, nt CO_2 läbiuhtumisega Tehnilise seguna võib kasutada põlevkivitootmise kõrvalprodukti, näiteks segu Honeyoli™ Aerogeeli inertses lämmastikukeskkonnas pürolüüsides saadakse süsinikaerogeel

(57) 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 Honeyol™ 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 III

Peikolainen, A.-L., Pérez-Caballero, F., Koel, M. Low-density organic aerogels from oil shale by-product 5-methylresorcinol.- *Oil Shale* 2008, 25, 348-358.

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

A. -L. PEIKOLAINEN[*], F. PÉREZ-CABALLERO, M. KOEL

Institute of Chemistry, Tallinn University of Technology
Akadeemia tee 15, 12618 Tallinn, Estonia

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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[*] Corresponding author: e-mail *annaliisa@gmail.com*

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-methylresorcinol (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 supercritical 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-methylresorcinol 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 conditions (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.

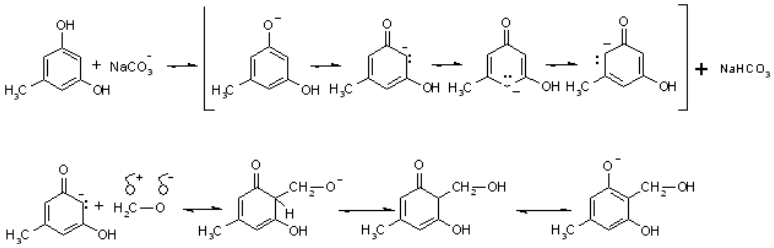

Fig. 1. Addition of formaldehyde to 5-methylresorcinol in the presence of basic catalyst (Na_2CO_3).

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**

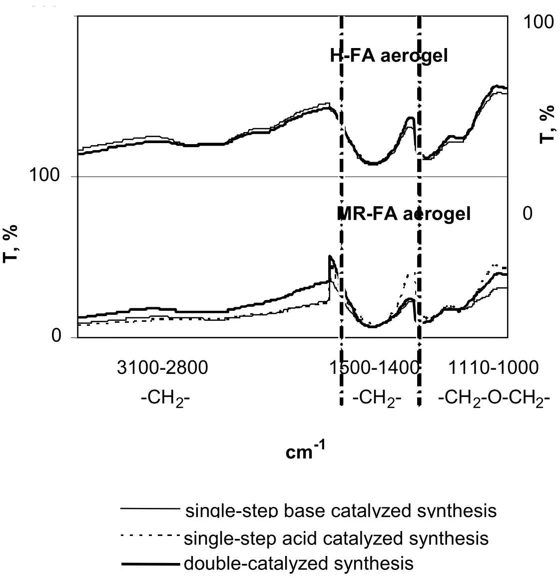

Fig. 2. MR-FA and H-FA aerogels via single- or double-catalyzed synthesis.

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.

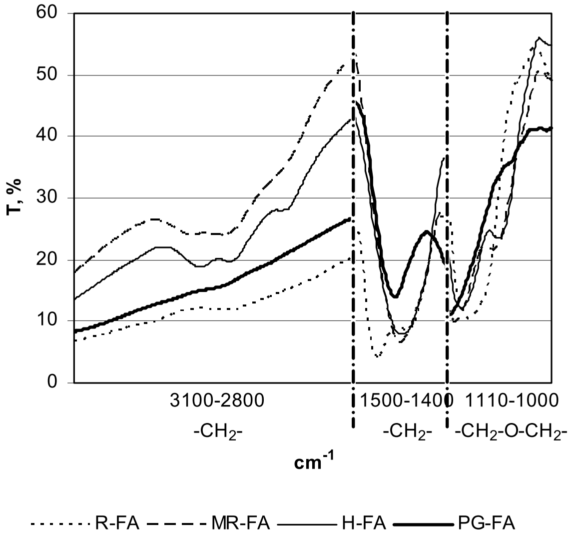

Fig. 3. IR spectra of MR-FA, H-FA, R-FA and PG-FA gels with bands of methylene and ether bridges.

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 polycondensation 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).

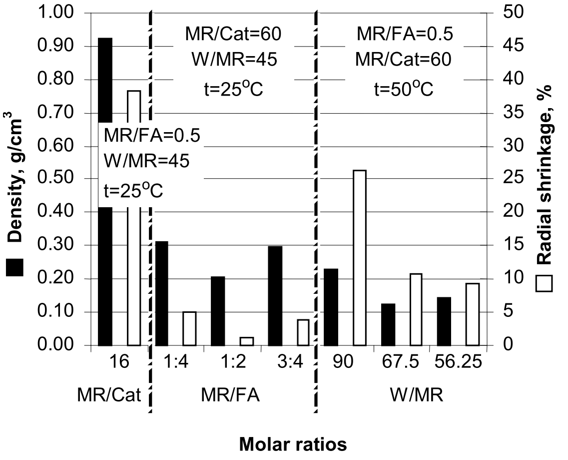

Fig. 4. Densities and radial shrinkages of SCE MR-FA aerogels according to molar ratios.

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.

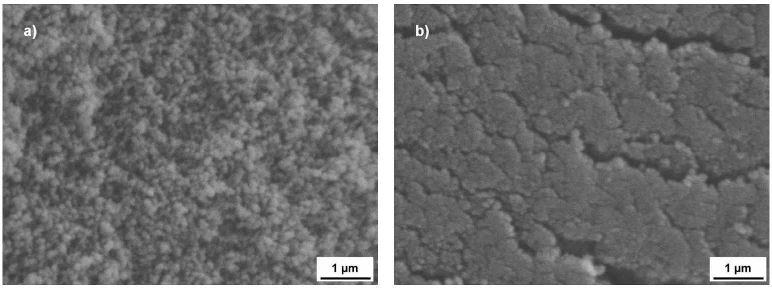

Fig. 5. Effect of supercritical fluid drying on the gel structure. MR-FA gel (MR/FA = 0.75) dried a) by SCE; radial shrinkage 4% and b) in ambient conditions; radial shrinkage 33%.

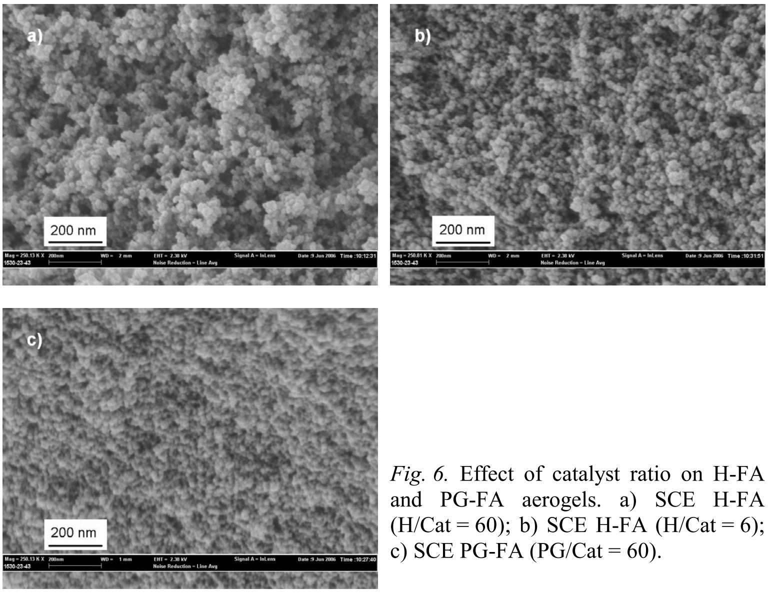

Fig. 6. Effect of catalyst ratio on H-FA and PG-FA aerogels. a) SCE H-FA (H/Cat = 60); b) SCE H-FA (H/Cat = 6); c) SCE PG-FA (PG/Cat = 60).

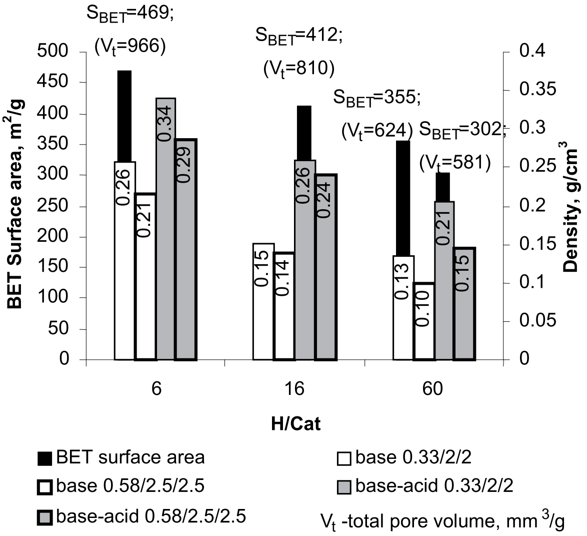

Fig. 7. Influence of catalysts and SCE regime on density, surface area and total pore volume of H-FA aerogels.

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).

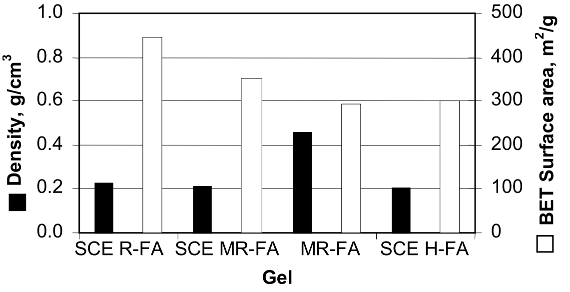

Fig. 8. Densities and BET surface areas of supercritically dried (SCE) R-FA, MR-FA, H-FA aerogels (catalyst ratio 60) and of MR-FA aerogel dried under ambient conditions.

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 conditions 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.

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Publication IV

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

F. Pérez-Caballero[a], A-L Peikolainen[*,a], M. Koel[a], M. Herbert[b], A. Galindo[b] and F. Montilla[b]

[a]*Institute of Chemistry, Tallinn University of Technology. Akadeemia tee 15, 12618 Tallinn, Estonia*

[b]*Departamento de Quimica Inorgɨnica, Universidad de Sevilla, Aptdo. 1203, 41071 Sevilla, Spain*

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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*Address correspondence to this author at the Institute of Chemistry, Tallinn University of Technology. Akadeemia tee 15, 12618 Tallinn; Tel: +372 620 4325; Fax: +372 620 2828; E-mail: annnaliiisa@gmail.com

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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) hexafluoroacetylacetonate [$Pd(C_4HF_6O)_2$] 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_2CO_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_2O 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 $\leq 3\%$. 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 ($-CH_2OH$) 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.

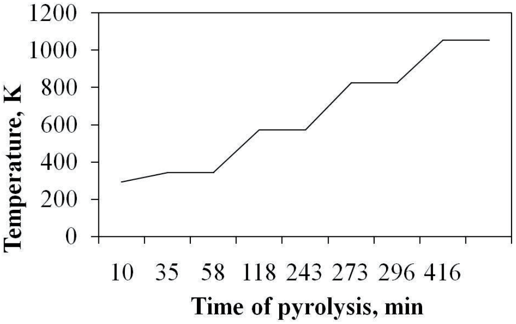

Fig. (1). The temprature program of pyrolysis.

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_2O 1	0.5	137.0	903.1	388.79	965.44	54.54	0.307	24.46
ACA-H_2O 2	2	198.5	NA$^+$	563.22	1018.96	73.09	0.311	25.09
ACA-H_2O 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**).

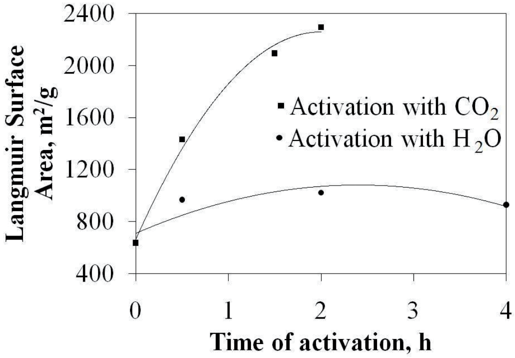

Fig. (2). The Langmuir surface area of the samples under study activated with both water and carbon dioxide.

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.

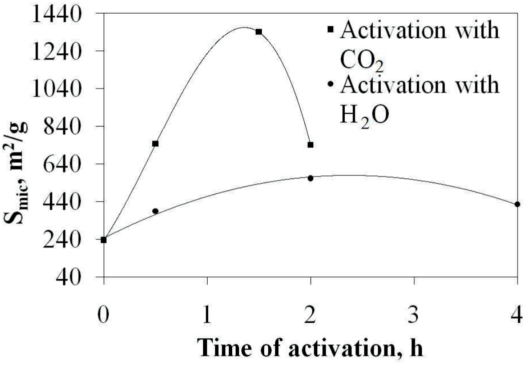

Fig. (3). Microporous area versus time of activation.

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.

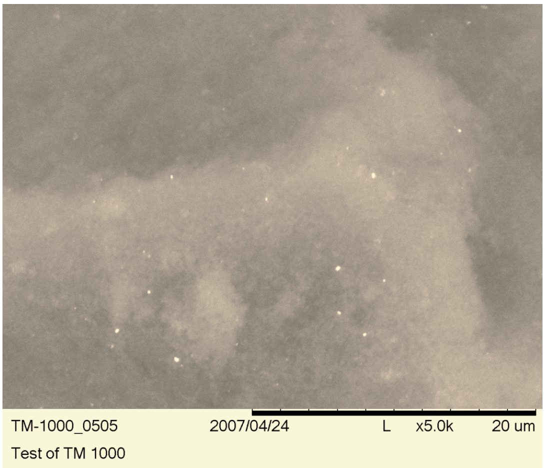

Fig. (4). A SEM image of the piece of carbon aerogel impregnated with black palladium.

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 V

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Organic acid catalyzed synthesis of 5-methylresorcinol based organic aerogels in acetonitrile

Anna-Liisa Peikolainen · Olga Volobujeva ·
Riina Aav · Mai Uibu · Mihkel Koel

Abstract A method of preparing 5-methylresorcinol and formaldehyde based organic aerogels in non-aqueous media with a benzoic acid derivative as a catalyst is being proposed in this paper. Here acetonitrile is used as a solvent that allows direct drying with carbon dioxide over the supercritical state without the need for a solvent exchange. The acidic properties of 2,6-dihydroxy-4-methyl benzoic acid promote the reaction of sol–gel polymerization, and at the same time it takes part in the reaction as a co-monomer and influences the nanostructure of the material. The evolution of the polymer was monitored using nuclear magnetic resonance spectroscopy and the structure of the resulting organic aerogels depending on the molar ratio of 5-methylresorcinol to 2,6-dihydroxy-4-methyl benzoic acid was studied by nitrogen adsorption–desorption measurements, scanning electron microscopy and infrared spectrometry.

Keywords Aerogel · Organic aerogel · 5-methylresorcinol · 2,6-dihydroxy-4-methyl benzoic acid · Supercritical drying · Oil-shale

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A.-L. Peikolainen (✉) · R. Aav · M. Koel
Department of Chemistry, Tallinn University of Technology,
Akadeemia tee 15, 12618 Tallinn, Estonia
e-mail: annnaliiisa@gmail.com

O. Volobujeva
Department of Materials Science, Tallinn University
of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

M. Uibu
Laboratory of Inorganic Materials, Tallinn University
of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

1 Introduction

Organic aerogels are precursors for the preparation of carbon aerogels, which are highly nanoporous materials with large specific surface areas. Their porous structure of interconnected pores allows them to be used as adsorptive materials [1–3]; when doped with precious metal, carbon aerogels become catalyst carriers [4–6] and can be used as electrodes for electrical double-layer capacitors [7, 8] and fuel cells [9, 10]. Carbon aerogels are electrically conductive and can be used as electrodes for electrical actuators [11].

Well known is an organic aerogel preparation method described by Pekala [12], by which aerogels were prepared from resorcinol–formaldehyde gels that were formed in basic aqueous solution and dried by supercritical CO_2 extraction. Before the extraction water, which is poorly miscible with CO_2, was exchanged for acetone prior to drying. There are a few examples where, in order to simplify the procedure, CO_2 miscible alcohols have been used as solvents for gel formation [13, 14].

Mulik et al. have synthesized aerogels from resorcinol–formaldehyde under acid conditions (HCl) in acetonitrile. In their experiments, acetonitrile was exchanged for acetone prior to supercritical CO_2 drying. [15] Recently, the same group replaced HCl with hydrated metal ions as Brønsted acids for the catalysis of the resorcinol–formaldehyde gelation in acetonitrile/ethanol, resulting in interpenetrating networks of metal oxides and resorcinol–formaldehyde [16]. The mixed-gels were again solvent-exchanged with acetone, however, this work is conceptually analogous to the incorporation of the catalyst to the gel reported here. In accord with the study of A.W. Francis on phase equilibria of ternary systems with liquid carbon dioxide, acetonitrile and water [17], it is possible directly to apply CO_2 extraction to the gel that contains acetonitrile. This has been done by Willey et al. [18], who, in order to dry the humic acid gel, replaced the original solvent (water) in the gel by acetonitrile prior to supercritical CO_2 drying.

In our previous studies we have been concentrated on using 5-methylresorcinol (5-MR) for aerogel preparation [5, 19] where we have been successful in synthesizing the gels in water and in methanol in the presence of inorganic base catalysts. The scope of this work was to develop a simple and fast procedure for producing aerogels from 5-MR in acetonitrile (ACN)—a solvent that does not require solvent exchange prior to drying. In order to prevent inorganic impurities an organic catalyst was desired. Acetic acid [20], oxalic acid and *para*-toluenesulfonic acid [21] have been used in aqueous systems as catalysts for aerogel preparation earlier. Here we propose a different efficient acidic organic catalyst, 2,6-dihydroxy-4-methyl benzoic acid (dHMBA). dHMBA has a very similar molecular structure to the monomer, 5-MR, and for this reason we expected that that derivative of benzoic acid, besides being a catalyst, would also take part in the sol–gel polycondensation as a co-monomer. Therefore, dHMBA would get incorporated in the aerogel backbone and it would not have to be removed after gelation, thus eliminating any need for time-consuming post-gelation washes. To confirm this hypothesis, NMR spectra were gradually recorded during the gelation process. The amount of catalyst in the sol has been found to be very important in tailoring the structure of the resulting gel: an increase in the amount of the catalyst in the sol leads to smaller gel particles, smaller pores and a larger specific surface area [22–25]. To test the influence of the 5-MR/dHMBA ratio on gel formation and on the morphology of the resulting aerogel material, a series of organic aerogels from 5-MR and dHMBA were synthesized.

Also benzoic acid and alternative hydroxy derivatives of benzoic acid such as 4-hydroxybenzoic acid, 2,5-dihydroxybenzoic acid and 2,6-dihydroxybenzoic acid were tested as potential catalysts for gel preparation. A homogenous gel was obtained when dHMBA or 2,6-dihydroxybenzoic acid was used. Our further study was focused on the use of dHMBA because it led to substantially faster gelation compared to 2,6-dihydroxybenzoic acid.

2 Experiment

2.1 Materials

5-Methylresorcinol (99.6%) and 2,6-dihydroxy-4-methyl benzoic acid (>99%) are by-products of the local oil shale processing industry and were obtained from Carboshale OÜ, Estonia. Formaldehyde, 37 wt% solution in water (stabilized with 10–15% of methanol), was purchased from Sigma–Aldrich. Acetonitrile, HPLC grade, came from Rathburn Chemicals Ltd., Germany.

The supercritical extraction system with a double clamp autoclave, 100 ml in volume, was constructed by NWA Analytische Meßgeräte GmbH, Germany. CO_2 (99.8%) was obtained from AS Eesti AGA.

2.2 Analysis techniques

Infrared (IR) measurements were performed with a Spectrum BX FT-IR System (Perkin Elmer) in the 4,000 to 400 cm^{-1} range by the KBr disk method. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 800 Avance III NMR spectrometer. Solvent peaks of CD_3CN in ^{13}C (118.69 ppm) and ^{1}H (1.94 ppm) NMR were used as chemical shift references. The morphology of the materials was determined using a Zeiss ULTRA 55 high resolution scanning electron microscope (SEM), and nitrogen adsorption analyses were performed using a Sorptometer KELVIN 1042 built by Costech International. Helium was used as a carrier gas, nitrogen as the adsorptive gas. The specific surface area (S_{BET}) was calculated according to the Brunauer-Emmet-Teller theory. Shrinkage was calculated as a decrease in the cross-sectional area of the cylindrical gel monolith during drying (Eq. 1).

$$\text{Shrinkage, \%} = \frac{A_{gel} - A_{OA}}{A_{gel}} \times 100 \qquad (1)$$

A_{gel} and A_{OA} are the cross-sectional areas of the gel and the corresponding aerogel, respectively.

2.3 Aerogel preparation

Appropriate amounts of the aromatic precursors 5-MR and dHMBA were dissolved in acetonitrile, and a formaldehyde solution (in water) was added subsequently. The molar ratio of aromatic monomers to formaldehyde (FA) was fixed at 0.5 and the molar ratio of the solvent (H_2O in FA solution and ACN) to the aromatic monomers was kept at 50. The molar ratio of 5-MR to dHMBA was varied from 90 and 10 mol% (indicated as 90/10) to 25 and 75 mol% (indicated as 25/75) of the total molar amount of aromatic monomers in the sol, respectively. Sol–gel polycondensation occurred at 25 °C within 3 h, depending on the composition of the sol. Gel formation was affirmed by tilting the sol-filled test tube 45° while observing the movement of the surface of the sol.

After aging the gel a minimum of 24 h, it was removed from the test tube and placed directly into the autoclave, where the drying of the material resulted in an organic aerogel. An optimized three-step process was followed for drying. First, the gel was introduced to liquid CO_2 at a pressure of 200 bars at 25 °C for 20 min to fill the pores of the gel with liquid CO_2 and mix it with ACN. The exit valve of the autoclave was then opened and the internal pressure reduced to 100 bars, allowing the liquid CO_2 to flow through the gel at a constant 100 bars at 25 °C for 2 h to replace the mixture of CO_2 and ACN with CO_2. After replacement, the temperature inside the autoclave was raised to 45 °C and supercritical CO_2 extraction (SCE) was carried out for 2 h. The extraction was completed by depressurising the autoclave to atmospheric pressure, and then lowering the temperature in the autoclave to ambient temperature.

3 Results and discussion

The correlation between the ratio of 5-MR to dHMBA and the morphology of the resulting aerogel is complicated due to the dual role of dHMBA in the system. A detailed mechanism of electrophilic aromatic substitution on resorcinol is being proposed by Mulik et al. [15]. Under acidic conditions, the mechanism of polymer formation starts with protonation of formaldehyde followed by nucleophilic attack by the π-system of aromatic monomer. Reactive positions of the aromatic ring are the 2-, 4- and 6- positions in the case of the 5-MR ring, and the 3- and 5- ring positions in the case of dHMBA due to the electronic properties of the substituents. This substitution leads to the formation of hydroxymethylated monomers. Further condensation of the hydroxymethyl group with an unsubstituted site in the aromatic ring results in CH_2 bridge formation between the aromatic monomers [15].

The dual behaviour of dHMBA can be seen from the effect of the 5-MR/dHMBA ratio on the gel formation time (Fig. 1).

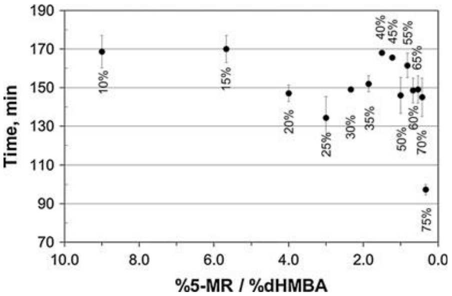

Fig. 1 Gel formation time at different %5-MR/%dHMBA ratios at 25 ± 1 °C (the exact value of %dHMBA is depicted next to each data point)

At lower dHMBA concentrations (10–25%) the speed of polycondensation increased as the amount of catalyst (dHMBA) was increased. At the same time, the increased amount of co-monomer (dHMBA) with two available reaction sites slows the formation of a solid cross-linked network. This effect could be noticed when the amount of dHMBA was increased from 25 to 40%. From 40% of dHMBA the rate of gelation again increased which may be related to the formation of a different type of polymer structure (shown below). The gel formation time as low as 97 min was achieved when the amount of dHMBA exceeded the amount of 5-MR three times.

The function of dHMBA as a monomer was tested by preparing a sol from dHMBA with FA in ACN without 5-MR in the mixture. A transparent yellow sol turned opaque in 1 h, but did not lead to the further formation of a solid gel network. This is probably because of the bifunctionality of dHMBA: it is able to form a linear polymer but not a three-dimensional network. The sample was dried under ambient conditions and the remaining solid was then analysed by IR spectrometry. In Fig. 2, the IR spectrum of the sample is compared to the spectrum of the gel from 5-MR and FA in water prepared according to a formula described by Pérez-Caballero et al. [26].

At wavenumbers 1470 and 2930 cm^{-1}, the absorption of C–H bonds from methylene bridges can be recognized, and the absorption at 1110 cm^{-1} corresponds probably to C–O bending vibrations of formaldehyde condensation products such as polymethylene glycol, hemiformal etc. [27], however, in the case of base-catalyzed 5-MR-FA aerogel the absorption could as well correspond to C–O from the methylene ether bridge linking the aromatic rings[28]. The absorption bands at 1680 cm^{-1} and 1200 cm^{-1} indicate the C=O and C–O bonds from carboxyl group of dHMBA, which are also present in the spectrum of pure dHMBA (Fig. 3).

The evolution of gel formation was monitored using NMR spectroscopy to confirm that dHMBA is a

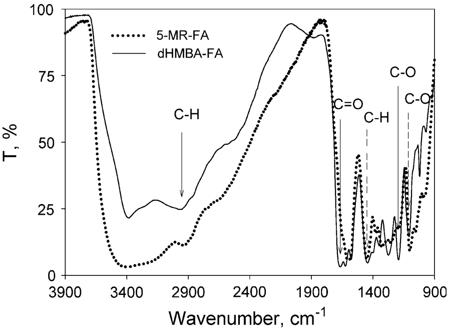

Fig. 2 IR spectra of 5-MR-FA and dHMBA-FA polymers

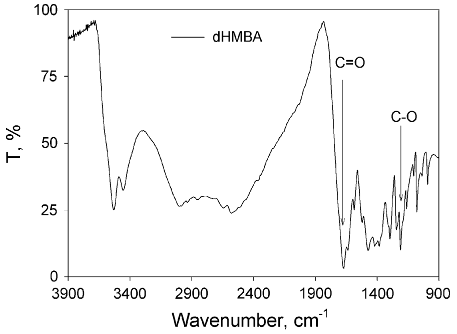

Fig. 3 IR spectrum of raw dHMBA

bifunctional molecule and that polymerization does not occur via the carboxyl group. A sample with a 5-MR/dHMBA molar% ratio of 50/50 was used. (Fig. 4) The spectra indicated as 0 min (^{13}C,^{1}H) were measured before adding FA solution to the sample, and the subsequent spectra were recorded during 142 (^{13}C NMR) and 120 (^{1}H NMR) minutes after the addition of FA. The polymerization proceeded during the NMR measurements. The formation of new compounds can be seen after the addition of FA and the disappearance of all aromatic signals within 2 h, only intermediates of the sol formation could be recorded in solution phase. The new signals on the spectra between 83–95 and 50–57 ppm are from FA solution and can be attributed to condensation products of FA and methanol. On the ^{13}C NMR spectra, the new signals of esters were expected to appear in the area of lower frequency than a signal of carboxylic carbon in parent acid (<172 ppm).

On the enlargement of the spectral fragment recorded after 35 min can be seen that the only new signals corresponding to the carboxylic carbons were resonating at higher frequency (173 ppm) than its parent acid. These signals can be attributed to newly formed carboxylic acids, which are intermediates of polymerization and the ester formation was not observed.

The same can be deduced from the ^{1}H NMR spectra (Fig. 5). All monomer peaks disappear within 2 h. It can also be followed that the acidity of the solution phase decreases during the reaction, as resonating frequency of protic hydrogens (a broad singlet) decreases from 4.3 (6 min) to 3.4 ppm (120 min). On the spectrum recorded before adding an aqueous solution of FA, the signals of hydrogens H3′ and H5′are overlapping with a signal from protic hydrogens (6.4 ppm). The signals at 4.6–4.9 and 3.3 and 3.4 correspond to hydrogens from FA and methanol polycondensates.

These results are in a good agreement with the gel formation time data. Also, faster consumption of 5-MR than dHMBA can be followed on ^{13}C and ^{1}H spectra, which is due to the deactivating influence of carboxyl group of dHMBA in aromatic substitution.

Measurements of nitrogen sorption on organic aerogels showed that an increase in the amount of catalyst increases the specific surface area of the material and the total volume of the pores only in the limited range of the dHMBA concentration. The largest specific surface area and the largest total pore volume, 600 m^2/g and 800 mm^3/g, respectively, were achieved at 5-MR/dHMBA ratio of 75/25 as can clearly be seen in Fig. 6. There were no micropores (pores with diameter less than 2 nm) in 5-MR-dHMBA-FA organic aerogels.

On SEM micrographs (Fig. 7), it can be seen that the morphology of the materials at ratios 75/25 and 25/75 are completely different. When the amount of 5-MR prevails, the structure of the aerogel is composed of uniform spherical clusters (diameters 24–25 nm), which is similar to that of 5-MR-FA aerogels prepared in basic aqueous

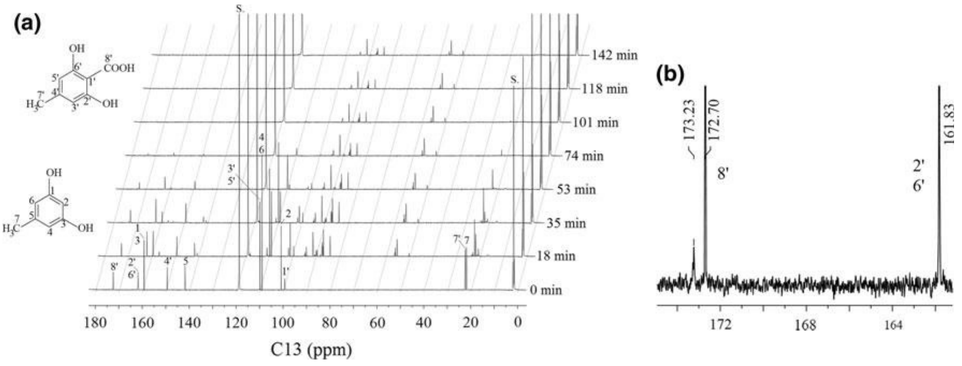

Fig. 4 **a** ^{13}C NMR spectra of 5-MR-dHMBA-FA sol in CD_3CN recorded during142 min after the addition of FA, **b** enlargement of the spectra recorded 35 min after the addition of FA; 200 scans per spectrum (201 MHz)

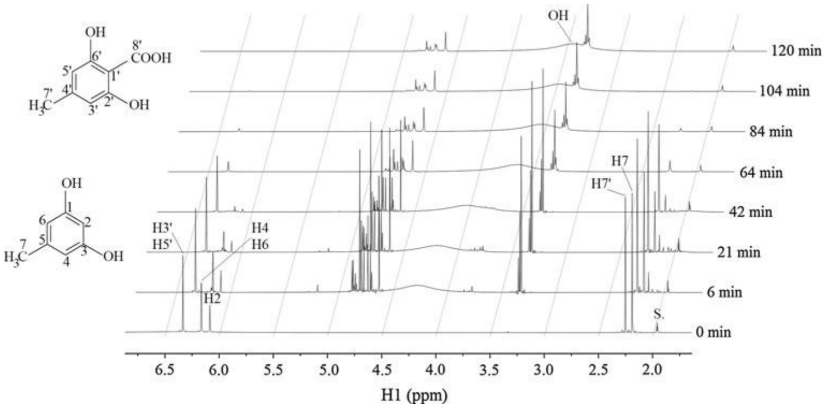

Fig. 5 ^{1}H NMR spectra of 5-MR-dHMBA-FA sol in CD_3CN recorded during 120 min after the addition of FA; 4 scans per spectrum (800 MHz)

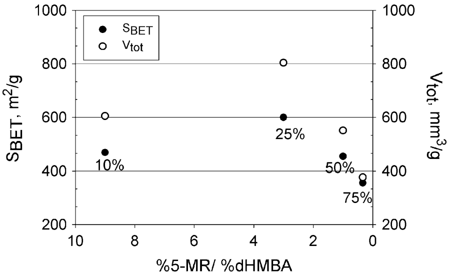

Fig. 6 Specific surface area (S_{BET}) and total volume of pores (V_{tot}) of aerogels with different ratios of %5-MR/%dHMBA (the exact value of %dHMBA is depicted next to the data point)

solvent [5]. Increasing the percentage of dHMBA led to the presence of large macropores due to the formation of strings of clusters. The strings of clusters with a broad size distribution can already be observed at a 5-MR/dHMBA ratio of 60/40 which correlates well with the results of gel formation time measurements. At 25/75, the cluster size distribution is again quite uniform, with diameters of approximately 15 nm. The morphology of aerogels 50/50 and 25/75 appears to be similar. The strings of clusters are longer with a higher amount of dHMBA, and the macropores are larger. Although the yellow colour of the sols intensified when the percentage of dHMBA was increased, all the gels in the examined range were transparent and equally bright orange in colour. After drying, the transparency remained to some extent, while aerogels with a higher percentage of 5-MR were darker than those with a higher percentage of dHMBA, the colour ranging from dark red to bright orange, respectively.

The densities of the materials correspond with the results of SEM analysis: by increasing the percentage of dHMBA in the sol, increasingly large macropores form in the gel and a material with a lower density is achieved (Fig. 8). Increasing macroporosity facilitates easy removal of the solvent from the gel leading to smaller shrinkage of the material during drying. However, from 5-MR/dHMBA ratio of 30/70 the density and shrinkage started to increase which is most likely due to increasingly tenuous network which is not supporting the overall shape of the monolith sufficiently. Aerogels become brittle. Along with the volume decrease during drying, the density of the aerogel increases.

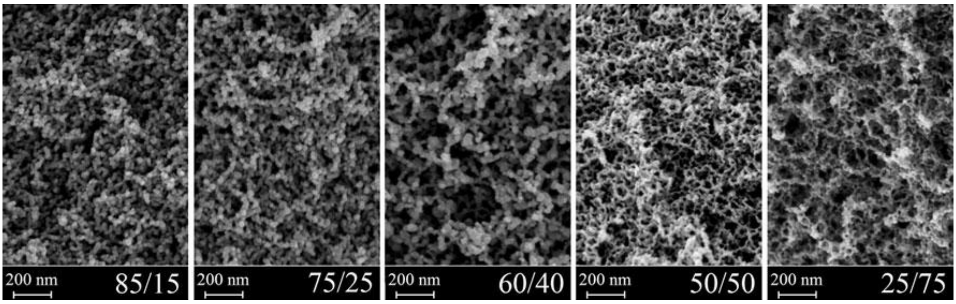

Fig. 7 SEM micrographs of aerogels prepared at different 5-MR/dHMBA ratios

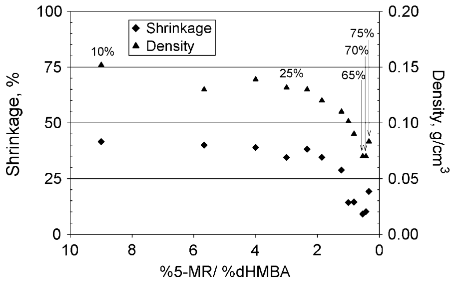

Fig. 8 Shrinkage during supercritical CO_2 drying and the densities of aerogels at different %5-MR/%dHMBA ratios

4 Conclusions

The 5-MR-dHMBA-FA system was found to be suitable for forming gels. The use of acidic organic co-monomer as a catalyst allowed producing organic aerogels free from inorganic impurities. Acetonitrile as a solvent enabled the material to be dried with supercritical carbon dioxide without the need of a solvent exchange prior to drying. This modification saves time and the consumption of organic solvents is substantially reduced. Because dHMBA has a dual role in polymerization, the ability to tune the specific surface area and porosity of an aerogel by varying the concentration of dHMBA in the sol is limited; however, it is important to study how this material behaves during pyrolysis, by which the organic aerogel will be turned into a usable carbon aerogel.

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CURRICULUM VITAE

1. Personal data

Name: Anna-Liisa Peikolainen
Date and place of birth: 10.11.1982, Rakvere, Estonia
Citizenship: Estonia

2. Contact

Address: Department of Chemistry, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia
Phone: +372 620 4359
e-mail: anna-liisa.peikolainen@ttu.ee

3. Education

2007-...	TUT, Chemistry and Gene Technology, doctoral studies
2005-2007	TUT, Applied Chemistry and Biotechnology, MSc degree
2005	TUT, Applied Chemistry and Biotechnology, BSc degree
2001-2005	TUT, Chemical and Materials Science, bachelor studies

4. Language competence

Estonian	fluent	French	basic skills
English	fluent	Finnish	basic skills
Russian	average		

5. Special courses

2010	“International Summer School on Aerogels”, German Aerospace Center DLR, Germany
2009-...	Graduate school “Functional Materials and Processes”. University of Tartu and Tallinn University of Technology
2008	Intensive course “Tenth Post-Graduate Summer School on Green Chemistry”. Interuniversity Consortium “Chemistry for the Environment”, Italy
2007-2008	Graduate school “New Production Technologies and Processes”. University of Tartu and Tallinn University of Technology

6. Professional experience

02/2009-...	Tallinn University of Technology, project assistant
03/2009-06/2009	Delft University of Technology (The Netherlands), the group of Prof. C.J. Peters
06/2003-07/2003	Rakvere Meat Processing Plant Ltd., quality control laboratory

7. Main areas of scientific work

Nanoporous materials, synthesis of organic and carbon aerogels.

8. Defended theses

Master’s thesis “Aerogels from 5-methylresorcinol and formaldehyde” (“Aerogeelid 5-metüülresortsinoolist ja formaldehüüdist”), 2007.

Bachelor’s thesis “Low density organic aerogels” (“Väikese tihedusega orgaanilised aerogeelid”), 2005.

ELULOOKIRJELDUS

1. **Isikuandmed**

Nimi:	Anna-Liisa Peikolainen
Sünniaeg ja -koht:	11.10.1982, Rakvere, Eesti
Kodakondsus:	Eesti

2. **Kontaktandmed**

Aadress:	Keemiainstituut, Tallinna Tehnikaülikool, Akadeemia tee 15, 12618 Tallinn, Eesti
Telefon:	+372 620 4359
E-posti aadress:	anna-liisa.peikolainen@ttu.ee

3. **Hariduskäik**

2007-...	TTÜ, Keemia ja geenitehnoloogia, doktoriõpe
2005-2007	TTÜ, Rakenduskeemia ja biotehnoloogia, loodusteaduse magistri kraad
2005	TTÜ, Rakenduskeemia ja biotehnoloogia, loodusteaduste bakalaureuse kraad
2001-2005	TTÜ, Keemia- ja materjaliteadus, bakalaureuseõpe

4. **Keelteoskus**

eesti keel	kõrgtase	prantsuse keel	algtase
inglise keel	kõrgtase	soome keel	algtase
vene keel	kesktase		

5. **Täiendusõpe**

2010	„International Summer School on Aerogels“, Saksamaa kosmoseuuringute keskus DLR, Saksamaa
2009-...	Doktorikool „Funktsionaalsed materjalid ja tehnoloogiad“. Tartu Ülikool ja Tallinna Tehnikaülikool
2008	Intensiivkursus „Tenth Post-Graduate Summer School on Green Chemistry“. Ülikoolidevaheline konsortsium „Chemistry for the Environment“, Itaalia.
2007-2008	Doktorikool „Uued tootmistehnoloogiad ja protsessid“. Tartu Ülikool ja Tallinna Tehnikaülikool

6. **Töökogemus**

02/2009-...	TTÜ, projekti assistent
03/2009-06/2009	Delfti Tehnikaülikool (Holland), Prof. C.J. Petersi grupp
06/2003-07/2003	Rakvere Lihakombinaat AS, kvaliteedikontrolli labor

7. **Teadustöö põhisuunad**

Nanopoorsed materjalid, orgaanilsed aerogeelid, süsinikaerogeelid

8. **Kaitstud lõputööd**

Magistritöö „Aerogeelid 5-metüülresortsinoolist ja formaldehüüdist“, 2007.

Bakalaureusetöö „Väikese tihedusega orgaanilised aerogeelid“, 2005.

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *NATURAL AND EXACT SCIENCES*

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