

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

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The objective of the present work was to prepare organic aerogels using a by-product of oil shale processing as a starting material. Low-density organic aerogels were synthesized via sol-gel polycondensation of formaldehyde (FA) and either 96% 5-methylresorcinol (MR) or the technical mixture named Honeyol™ (H) containing 59.6% of 5-methylresorcinol among other diphenolic compounds, using supercritical CO₂ 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/cm³ and specific surface area 350 m²/g. At the same molar ratios H-FA aerogel had 29% shrinkage, 302 m²/g specific surface area and the density as low as 0.10 g/cm³.

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

Introduction

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

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

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

Among other gel drying techniques (conventional drying, freeze-drying), supercritical fluid drying is preferred. At the supercritical state no meniscus is formed between gaseous and liquid phase and capillary pressures within the pores, causing the reduction of porosity or cracking the fragile gel skeleton during drying, are avoided. Resulting densities, specific surface areas and percentages of shrinkage differ accordingly to the fluid used. [6] CO₂ 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 CO₂ makes it environmentally friendly processing agent.

Experimental

Materials and equipment

5-Methylresorcinol of purity $\geq 96\%$ 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 Na₂CO₃ (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 Plock, 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. CO₂ (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) Na₂CO₃ 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 CO₂ (SCE) comprised of pressurization of CO₂ to 20 MPa at 25 °C, flowing liquid CO₂ through the gel at 12 MPa and 25 °C and supercritical CO₂ 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 Na₂CO₃ 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 (–CH₂OH) 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]. Na₂CO₃ 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 (–CH₂–) and methylene ether (–CH₂–O–CH₂–) 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.

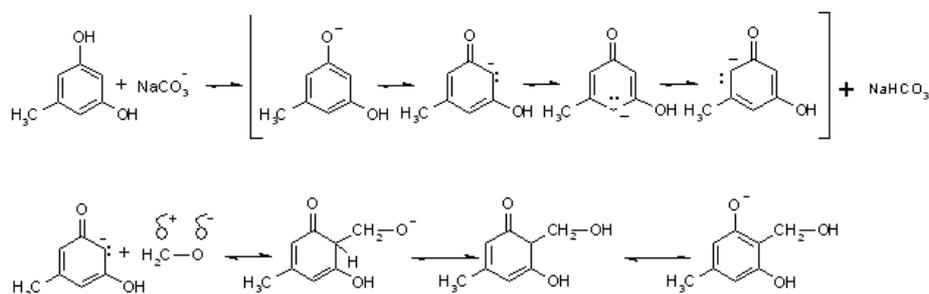


Fig. 1. Addition of formaldehyde to 5-methylresorcinol in the presence of basic catalyst (Na_2CO_3).

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

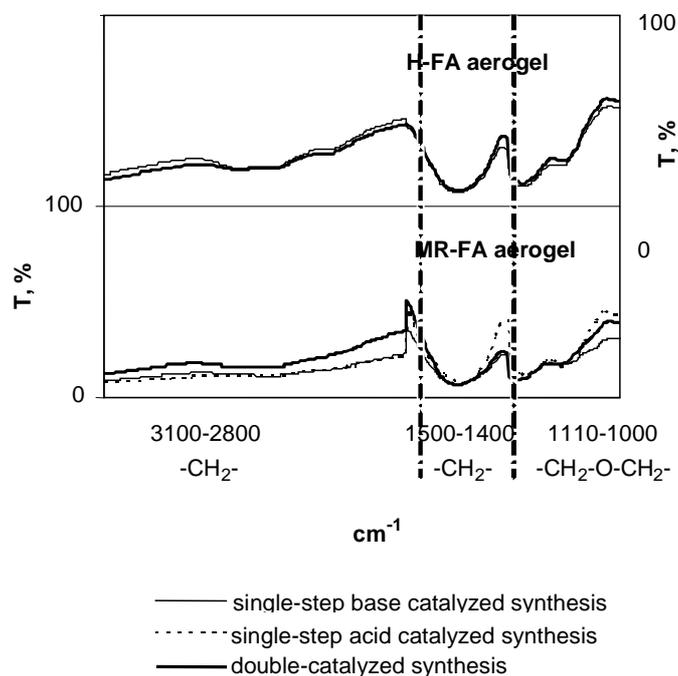


Fig. 2. MR-FA and H-FA aerogels via single- or double-catalyzed synthesis.

In the spectra IR adsorption bands of $-\text{CH}_2-$ (2930 cm^{-1} and 1450 cm^{-1}) and $-\text{CH}_2\text{-O-CH}_2-$ (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 $-\text{CH}_2\text{-O-CH}_2-$ 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* $-\text{CH}_2-$ bridges preferable compared to tri-substituted molecules where $-\text{OH}$ or $-\text{CH}_3$ groups at the same positions can be found.

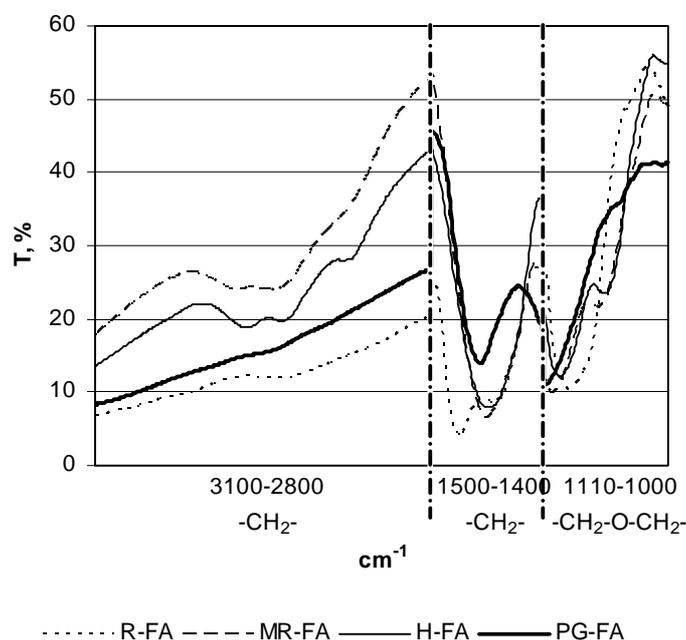


Fig. 3. IR spectra of MR-FA, H-FA, R-FA and PG-FA gels with bands of methylene and ether bridges.

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):

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

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).

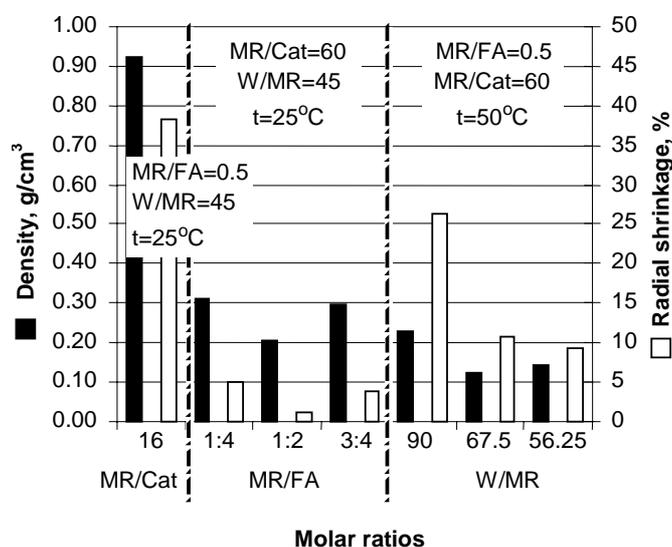


Fig. 4. Densities and radial shrinkages of SCE MR-FA aerogels according to molar ratios.

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 CO₂ 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/cm³. 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 $65 \text{ }^\circ\text{C}$ 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.

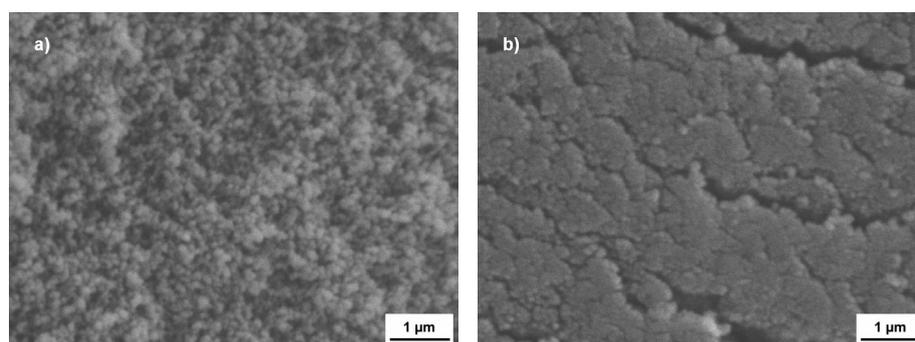


Fig. 5. Effect of supercritical fluid drying on the gel structure. MR-FA gel (MR/FA = 0.75) dried a) by SCE; radial shrinkage 4% and b) in ambient conditions; radial shrinkage 33%.

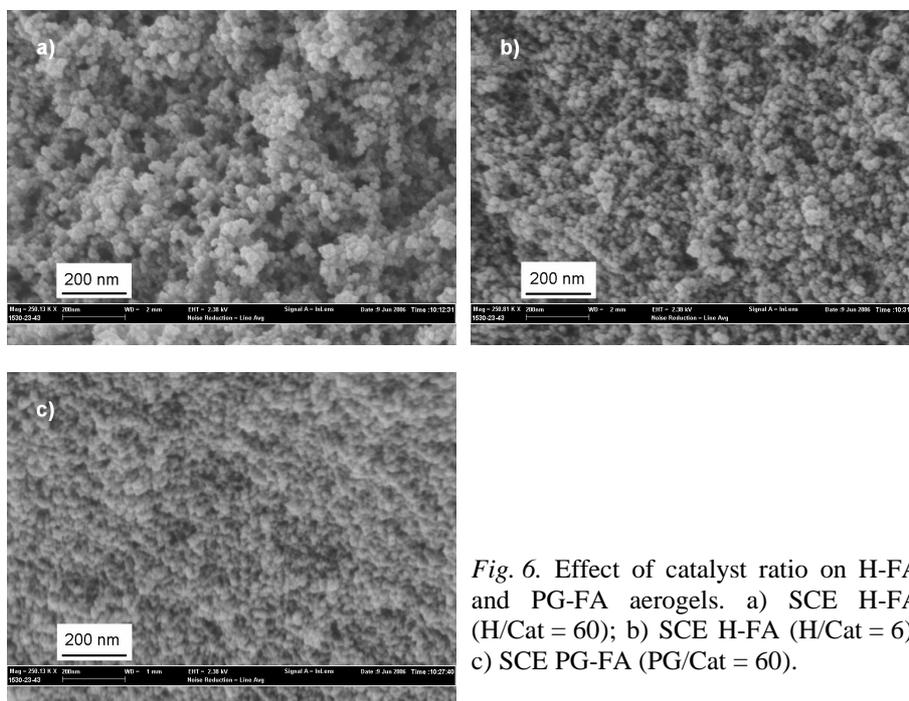


Fig. 6. Effect of catalyst ratio on H-FA and PG-FA aerogels. a) SCE H-FA (H/Cat = 60); b) SCE H-FA (H/Cat = 6); c) SCE PG-FA (PG/Cat = 60).

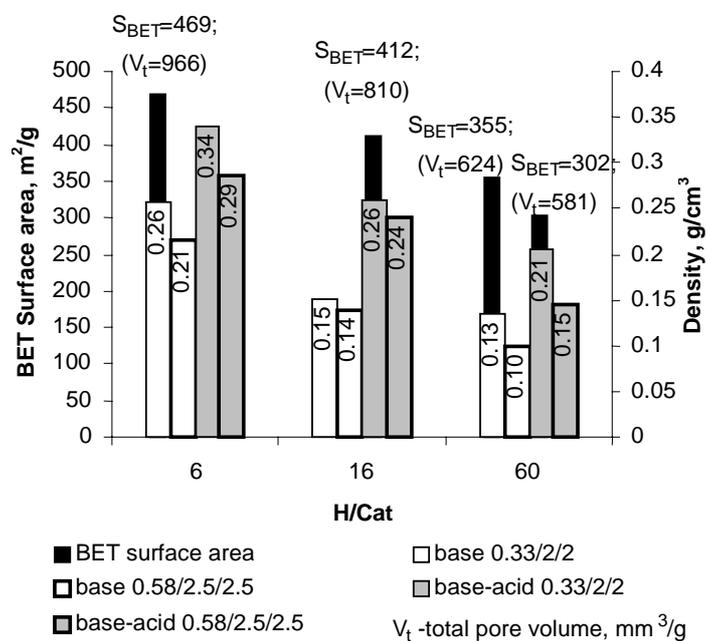


Fig. 7. Influence of catalysts and SCE regime on density, surface area and total pore volume of H-FA aerogels.

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).

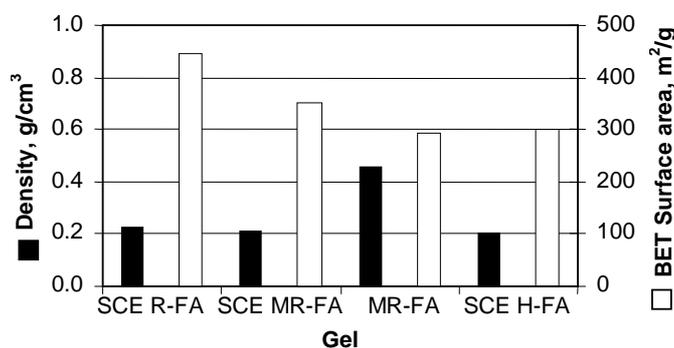


Fig. 8. Densities and BET surface areas of supercritically dried (SCE) R-FA, MR-FA, H-FA aerogels (catalyst ratio 60) and of MR-FA aerogel dried under ambient conditions.

Specific surface area is the largest for R-FA aerogel (455 m²/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 m²/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/cm³ and for H-FA 0.10 g/cm³. Preparation of MR-FA and H-FA aerogels is effective *via* the single-step base catalyzed synthesis requiring at least 10 times larger amount of catalyst than R-FA and PG-FA for gelation. Acid catalyst does not contribute to strengthening the gel structure and does not lead to desired lower densities. Supercritical condi-

tions are necessary for drying, especially for HoneyolTM-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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