

Preparation of Low-Density Aerogels from Technical Mixture of Diphenolic Compounds

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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. There is available the technical mixture of diphenolic compounds named Honeyol™ (H) containing 59.6% of 5-methylresorcinol.

Low-density organic aerogels were synthesized via sol-gel polycondensation of H and formaldehyde (FA) molecules, using supercritical carbon dioxide for drying the gel obtained. Polymerization of H and FA in the presence of potassium hydroxide as the base catalyst (C) was carried out in methanol at temperature 60°C. FA and KOH were dissolved in methanol as well. The use of methanol allows excluding the time consuming solvent exchange step from the process [1].

Porosity and particle characteristics of H-FA aerogels can easily be controlled by varying preparation conditions and concentrations of precursors. As a result of our research, it became evident that in case of H-FA aerogel single-step base catalyzed synthesis led to lower densities and higher BET surface areas and pore volumes compared to double-step base-acid catalysis. The lowest density was achieved for H-FA aerogel with molar ratios H/FA=0.5, methanol/H=45 and H/C=60 (moles of H is calculated as the amount of 5-methylresorcinol in Honeyol™). Gelling time of 8 days and less than 6h CO₂ processing resulted in an aerogel with density 0.10 g/cm³. In order to decrease aerogel preparation time, the amount of catalyst was increased: solution with catalyst ratio H/C=6 gelled within one day having BET surface area 469 m²/g and total pore volume 966 mm³/g after drying, the density, however, increased.

Examination of the obtained materials was carried out by means of scanning electron microscopy, infrared spectroscopy, nitrogen adsorption-desorption analysis and linear measurements.

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 with low density and high specific surface area. Carbon aerogels can be used as adsorbents, membranes and carriers for metal catalysts; they find application in high-energy physics and acoustic technology; low thermal conductivity allows usage as thermal insulators. Carbon aerogels also find application as electrode materials because of their controllable porous structure and electrically conductive network [2].

The most well-studied aerogel preparation method invented by Pekala uses resorcinol (R) and formaldehyde as precursors [3]. The gel is produced via the double-catalyzed base-acid synthesis and after the solvent exchange step the drying of the gel is carried out with CO₂ at its supercritical conditions to prevent the capillary pressures from breaking the gel's structure. In our research the technical mixture of diphenolic compounds named Honeyol™ was used instead of resorcinol. Honeyol™ is a by-product in oil shale industry and this makes it a cheap material at the region where oil shale industry is active. Honeyol™ contains 59.6% 5-methylresorcinol. As an aerogel preparation from purified 5-methylresorcinol was carried out successfully [4], it was decided to find a method for preparing aerogels from the technical mixture without prior purification.

MATERIALS AND METHODS

Honeyol™ which is a product of Viru Keemia Grupp, Estonia, was obtained from Institute of Oil Shale at Tallinn University of Technology; potassium hydroxide was from Chemapol Lachema Brno, Czech Republic; formaldehyde was in the form of 35% 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 HPLC reagent, Rathburn Chemicals Ltd., Scotland.

Thermostat for gelation: TECHNE Dri-Block® DB 3A, Spain; supercritical drying was performed on self completed equipment consisting of High Pressure Pump HPP 4001, Czechia, thermostat: Intersmat IGC 121 C FL, France, and in laboratory constructed high pressure cell with volume of 10 mL. CO₂ was from Eesti AGA with purity 99.8%.

The preparation of the organic aerogel was started from the sol preparation. First, Honeyol™ and KOH were separately dissolved in methanol, and then the solutions of Honeyol™, KOH and formaldehyde were mixed. The gelation of the sol was carried out in test tubes at 60°C. After the gels were formed, the gel rods were removed from the test tubes and placed into the extractor for drying in the supercritical CO₂ flow. The regime of drying (SCE) comprised of pressurization of CO₂ to 20MPa at 25°C, flowing liquid CO₂ through the gel at 12MPa and 25°C and supercritical CO₂ extraction at 12MPa and 50°C.

RESULTS

At the beginning of the polymerisation the addition of formaldehyde to the aromatic ring results in the formation of hydroxymethyl groups (-CH₂OH). 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 formaldehyde takes place. Honeyol™ contains dihydroxy benzenes (**Table 1**) with the additional substitutions at the positions where the directing groups would affect FA to react on, causing some changes in gel preparation compared to 5-methylresorcinol (pure)-formaldehyde gel (MR-FA). [4]

Table 1 Honeyol™ composition

| Component | mass fraction, % |
|-----------------------------|------------------|
| 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 |
| Not identified | 3,6 |
| Dihydroxy benzenes | 99,2 |

In case of Honeyol™, the common conditions like Na₂CO₃ as the catalyst, water as the solvent and room temperature for gelation did not lead to gel formation. The gel, however, formed when the amount of catalyst and the gelation temperature were increased. After curing the gel piece in the acidic media (acetic acid solution, pH~4) as the second step of the double-catalyzed synthesis, and the transfer to the acetone for the solvent exchange step, the dissolving of the gel piece started. The gel remained intact when methanol, which is also miscible with CO₂, was used for the solvent replacement instead of acetone. Further, methanol was used as the original solvent following the examples from the literature [5] to eliminate the need of the solvent exchange and shorten the aerogel preparation process. KOH was used in the role of the basic catalyst, because Na₂CO₃ is poorly soluble in alcohol. KOH being the stronger base than Na₂CO₃, it could also be used in smaller amounts.

The sol prepared using the molar ratios H/FA=0.5, methanol/H=45 and H/C=60 turns into the gel after curing it 8 days at the temperature of 60°C, but as the gelling time is strongly dependent on the amount of catalyst in the sol, that time can be shortened to 1 day by decreasing the ratio H/C about 10 times.

For resorcinol-FA aerogels the double-catalyzed synthesis has been proven to be more efficient in the aspect of bond formation between resorcinol molecules leading to smaller shrinkage and lower aerogel densities compared to the gels synthesized with basic catalyst only [6]. The H-FA gels prepared by single-step base catalysis and double-catalyzed synthesis were compared by the means of IR spectra measurements (Spectrum BX FT-IR System (Perkin Elmer)). In the spectra IR absorption bands of $-\text{CH}_2-$ (2930cm^{-1} and 1450cm^{-1}) and $-\text{CH}_2\text{-O-CH}_2-$ (1100cm^{-1}) bonds in H-FA aerogels formed via the single-step base catalyzed and double-catalyzed synthesis almost overlap, therefore, the use of only base catalyst was considered sufficient.

It is known that in the presence of acid catalyst, in methanol unreacted formaldehyde leads to the formation of hemiformal [7], hindering further cross-linking between the molecules, causing 20-30% shrinkage for H-FA aerogels while supercritical drying. Taking into account the results of IR spectra measurements and excluding the step of catalyzation in acidic media, it was possible to shorten the aerogel preparation time by several days.

The comparison of the absorption bands caused by methylene and ether bridges between the aromatic molecules in SCE dried R-FA, MR-FA and H-FA aerogels is shown on **Fig.1**.

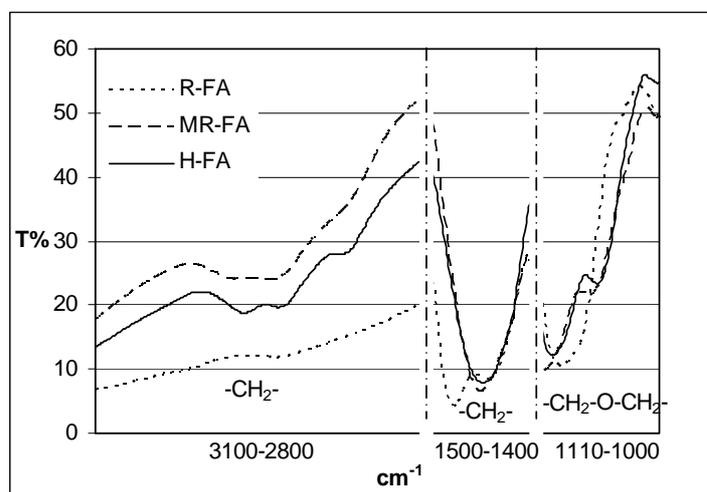


Figure 1 IR absorption of methylene and ether bridges in R-FA, MR-FA and H-FA aerogels

From this figure can be seen that the gels from both, di-substituted and tri-substituted aromatic precursors have the similar amount of $-\text{CH}_2\text{-O-CH}_2-$ bridges between the molecules, showing the equal absorption band at 1100cm^{-1} . Methylene bridges at their characteristic wavenumbers (2930cm^{-1} and 1450cm^{-1}) show stronger absorption for R-FA aerogel than for MR-FA and H-FA aerogels. Originally the resorcinol molecule has no substitutions in the 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 $-\text{CH}_3$ group at this positions can be found.

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

$$\text{Shrinkage}_{\text{radial}} [\%] = \frac{\varnothing_{\text{before}} - \varnothing_{\text{after}}}{\varnothing_{\text{before}}} * 100\% \quad (1)$$

It is known that the number of FA molecules as a cross-linking agent must exceed the number of aromatic molecules to form three dimensional mesoporous material [3], however, formaldehyde remaining in the gel after polycondensation could induce a collapse of the mesoporous structure and decrease the volume of the mesopores in the aerogel prepared [8]. Following this, the H/FA molar ratio was kept 1:2; methanol/H ratio used was 45. The catalyst amount in the sol was varied to observe its influence on the size of aerogels' particles and pores, the density and on the radial shrinkage. The SEM images (Leo Supra 35 Scanning Electron Microscope) of H-FA aerogels with H/C ratios 60 (**Fig.2a**) and 6 (**Fig.2b**) show that the increase in the amount of the catalyst leads to smaller particles and also smaller pores.

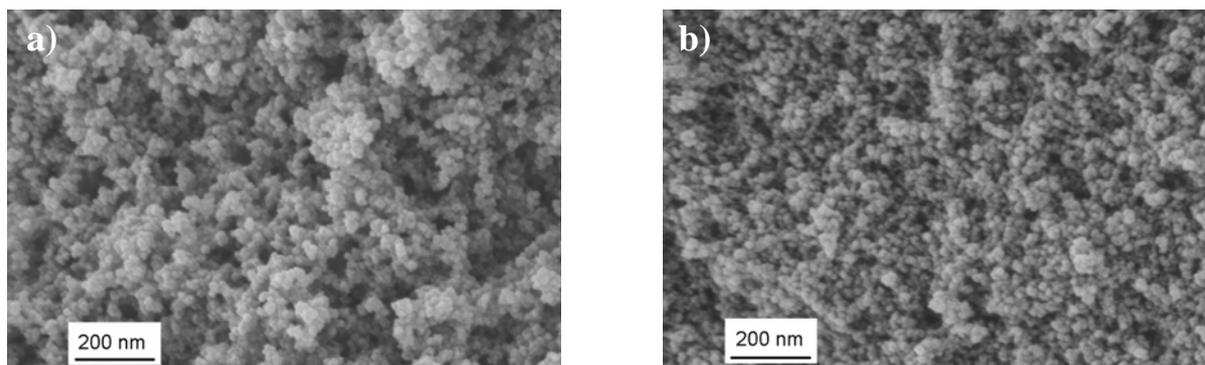


Figure 2 Effect of the catalyst amount on supercritically dried H-FA aerogels. a) H/C=60; b) H/C=6

H/C ratio 6 leads to transparent gels with the particle size of 10nm; the gels with the H/C ratio 60 are opaque and have more than 20nm sized particles. Pore size distribution for unpyrolyzed organic aerogels is wide and no micropores were detected with nitrogen adsorption measurements (Sorptionmeter KELVIN 1042 built by Costech International).

The fact that increasing the amount of the catalyst leads to higher density [3], larger total pore volume and larger BET surface area is known for R-FA aerogels [8,9,10] and can also be noticed in case of Honeyol™ - **Fig.3**. On the diagram, the gels prepared by the single-step base catalyzed and by the double-step base-acid catalyzed synthesis were compared: the density is lower, the specific surface area is larger and the total pore volume higher when the single step base catalyzed synthesis is used.

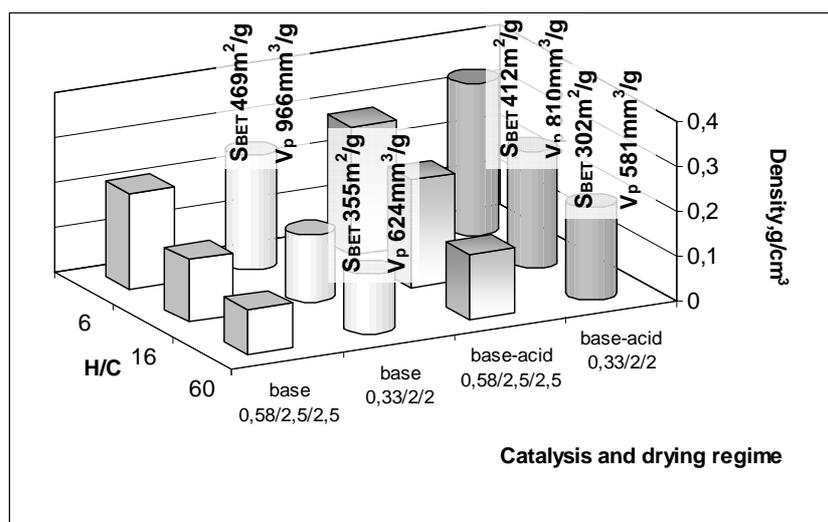


Figure 3 The influence of the catalysis and SCE regime on the density, the specific surface area and on the total pore volume of H-FA aerogels. The drying regime is expressed by three numbers which describe the time (h) of each step of the CO₂ processing.

The calculations of linear shrinkage (1) for both, single- and double-catalyzed gels, however, do not show significant difference, so we assume that the increase in density occurred during aging in acidic media and not due to the shrinkage while supercritical drying. It is interesting to note that although the catalyst amounts were varied, in case of H-FA aerogels the percent of the linear shrinkage seemed unaffected by it- regardless of increase or decrease of the catalyst amount in the sol, the aerogel always shrank 20-30% during the drying process.

The density of H-FA aerogels is seriously 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 carry out all the water from the pores. For H-FA the density 0.10g/cm³ was the lowest achieved with the single-step base catalyzed synthesis (H/C=60) and 5h and 35min supercritical drying. Extending the drying time further, even less dense aerogels could likely be obtained.

On **Fig.4**, the densities and the specific surface areas of aerogels prepared from different aromatic precursors (resorcinol, 5-methylresorcinol and Honeyol™) via double-catalyzed synthesis are compared. The gels were prepared using equal molar ratios (R/FA=MR/FA=H/FA=0.5; W/R=W/MR=Met/H=45; R/C=MR/C=H/C=60) and for drying the similar supercritical conditions were applied.

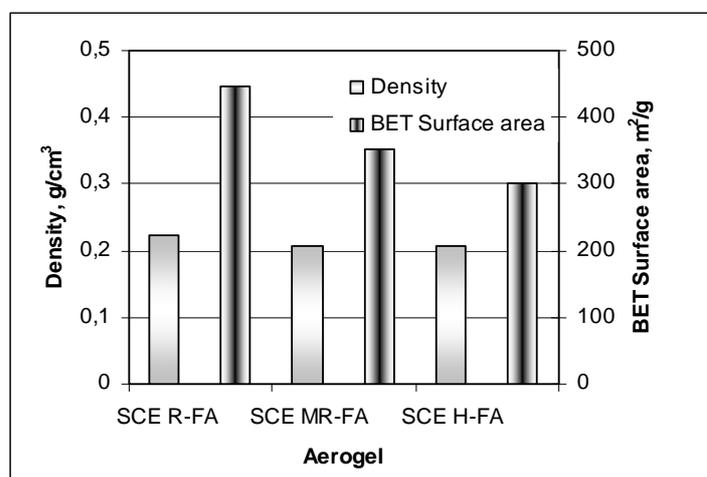


Figure 4 Densities and BET surface areas of supercritically dried (SCE) R-FA, MR-FA, H-FA aerogels (H/C= 60)

The specific surface area, calculated by BET theory, is the largest for the R-FA aerogel (455m²/g), for the aerogel from 5-methylresorcinol it is slightly smaller. Although at these conditions the specific surface area for H-FA aerogel is the smallest, from Honeyol™ we have obtained aerogels with larger surface area than presented on this figure. It must be mentioned that drying R-FA and MR-FA at room temperature and pressure resulted in higher density and decreased specific surface area. In case of H-FA gels, the BET surface area was not measured as the gel rod cracked into pieces due to the capillary pressures showing the importance of the supercritical fluid drying during the aerogel preparation process.

CONCLUSION

Honeyol™ is a very competitive precursor beside well-studied resorcinol allowing easily control aerogels structure by the same techniques, resulting in very similar characteristics such as the porous structure, low density and high specific surface area. Preparation of H-FA aerogel is effective via the single-step base catalyzed synthesis - acid-catalyst does not contribute to strengthening the gel structure and does not lead to desired lower densities as smaller shrinkages as was found in the current study. Supercritical conditions are necessary for drying H-FA gels, which do not survive the capillary

pressures and crack when dried at ambient conditions; however, drying times for obtaining the gel with competitive densities are extremely short.

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