

Preparation of Organic Aerogels

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ABSTRACT

Preparation of low-density methylresorcinol-formaldehyde (MR/FA) organic aerogels by supercritical carbon dioxide drying is reported. Double catalysed synthesis leads to quickly gelating and homogeneous gels that can be dried supercritically within 3.5 hours without significant shrinkage during the process. Optimal ratios for the lowest density and minimum shrinkage are MR/FA=0.5, MR/C=60 (C-catalyst) and W/MR=45 (W-water). Basic catalyst used in this work is sodium carbonate, and acetic acid as acid catalyst is used after gelation in basic conditions. Water in gel is exchanged for acetone before supercritical CO₂ drying by changing the solvent 3 to 5 times. In this case supercritical extraction is very short in comparison with extractions lasting 8 hours to 3 days with aerogels made of alternative precursors, still having large shrinkage. Resulting density for methylresorcinol-formaldehyde aerogel is as low as 0.2g/cm³. For even greater pore volume 5 hour CO₂ processing is enough. It is also found that aerogel prepared by using acid catalyst only can be ambient dried without any shrinkage, but density of the aerogel is then 0.9g/cm³ and homogeneity of the aerogel is unsatisfying.

Difference between methylresorcinol-formaldehyde aerogel and previously studied phenol-formaldehyde and resorcinol-formaldehyde aerogels is the transparency of the gel. In case of methylresorcinol much more catalyst must be used to obtain a transparent gel. Then the shrinkage during supercritical processing is also greater. Examination of the materials obtained is carried out by means of scanning electron microscopy, infrared spectroscopy and linear measurements.

INTRODUCTION

Gel is composed of solid and liquid phase, which are independent of each other. If the liquid phase could be removed from the gel in a non-destructive manner, a solid porous material would be left with approximately the same shape and volume as the original gel. In practice supercritical extraction (SCE) is used for drying gels, because evaporation of liquids from gels resulted in large capillary pressures within the pores from surface tension caused by the receding liquid meniscus. This is leading to reduced porosity (~50%) or cracking fragile solid skeleton. [1] The main purpose of this work was preparation of methylresorcinol-formaldehyde organic aerogel via supercritical extraction. Methylresorcinol is a cheap precursor in Estonia as it is by-product in fossil fuel production. To gain the lowest density and minimum shrinkage, molar ratios of reagents and experiment conditions had to be varied. Although no publications about MR on this theme were found, the similarity to processes with resorcinol (R) and phenol (P) has been assumed.

MATERIALS AND METHODS

The first step is preparation of colloidal solution where formation of chemical and physical structure of polymer takes place. Concentrations of reactants are presented in molar ratios: R/FA, R/C, W/R. Formaldehyde is responsible for crosslinking aromatic molecules, therefore there must be at least two times more of FA than R. Too much formaldehyde remaining

induces a collapse of mesopore structure and decreases pore volume of the aerogel prepared.[2]

Amount of catalyst in solution affects particle size and also transparency of gel. Increasing the amount of catalyst decreases the size of particles.[3] More catalyst leads to faster gelation.[4] The compression modulus of gels synthesized at different catalyst level show a trend in which a higher modulus is obtained at high catalyst level.[5]

W/R describes the amount of solid fraction in gel. Increasing solid fraction (R) leads to larger pores and quicker gelation.[4]

Basic or acid catalyst can be used for preparing gel, but double-catalysed synthesis is considered to be most effective. Under basic conditions, formaldehyde links quickly to phenolates to form methylol (-CH₂OH) groups. The second acid catalyst step promotes polycondensation.[6] As for the basic catalysts, it has been shown that the valence and ionic radius of hydrated cations affect the changes of species in the reaction medium, rate constant depends on it also.[7] Beside hydroxides, carbonates are used as basic catalysts.

Usual gelating temperature used in case of resorcinol is 50-90°C. The higher is the temperature, the faster gelation occurs.[4]

It is important to remove all of the liquid phase from gel during SCE and it is said to be very time consuming process.

Three different precursors were used in this work: ≥99% resorcinol (product of Aldrich), 96% 5-methylresorcinol and 59.6% methylresorcinol (Honeyol) (products of Oil-Shale Institute of Tallinn University of Technology); formaldehyde (35% w/w solution). Experiment conditions are given in **table 1**.

Table 1 Synthesis conditions of resorcinol- and methylresorcinol-formaldehyde organic aerogels

Experiment no.	Molar ratios				Gelating temperature [°C]	Aging time [days]		Times of exchanging acetone	Time of SCE [hours]		
	MR/FA	MR/C	C	WWR		Basic conditions	Acidic conditions		20 MPa, 25 °C	12 MPa, 25 °C	12 MPa, 50 °C
8	0,25	60	Na ₂ CO ₃	45	25	9	6	7	0,38	2,5	2
9	0,5	60	Na ₂ CO ₃	45	25	9	6	7	0,38	2,5	2
10	0,75	60	Na ₂ CO ₃	45	25	9	6	7	0,38	2,5	2
11	0,5	60	Na ₂ CO ₃	90	50	40	6	5	0,38	2,5	2
12	0,5	60	Na ₂ CO ₃	67,5	50	13	6	5	0,38	2,5	2
13	0,5	60	Na ₂ CO ₃	56,25	50	11	6	5	0,38	2,5	2
14	0,5	60	Na ₂ CO ₃	45	25	2	6	5	0,38	2,5	2
15	0,5	60	Na ₂ CO ₃	45	25	2	6	5	0,38	2	2
16	0,5	60	Na ₂ CO ₃	45	25	2	6	5	0,38	1,5	2
17	0,5	60	Na ₂ CO ₃	45	25	2	6	5	0,38	1	2
18	0,5	100	Na ₂ CO ₃	45	25	23*					
19	0,5	200	Na ₂ CO ₃	45	25	23*					
20	0,5	300	Na ₂ CO ₃	45	25	23*					
21	0,5	60	CH ₃ COOH	45	25	9	5 (water)	5	0,38	2,5	2
22	0,5(59,6)	60	Na ₂ CO ₃	90	50	42*					
23	0,6(R)	60	Na ₂ CO ₃	45	25	2	6	5	0,38	2,5	2
24a	0,5	16	Na ₂ CO ₃	45	25	5	5	5	0,38	2	6
24b	0,5	16	Na ₂ CO ₃	45	25	6	6	5	0,38	2,5	2

*did not gelate during the time shown in the table

(=water)-gel is aged in water instead of acid

(59,6)- 59,6% methylresorcinol is used instead of 96% methylresorcinol

(R)-resorcinol is used instead of methylresorcinol

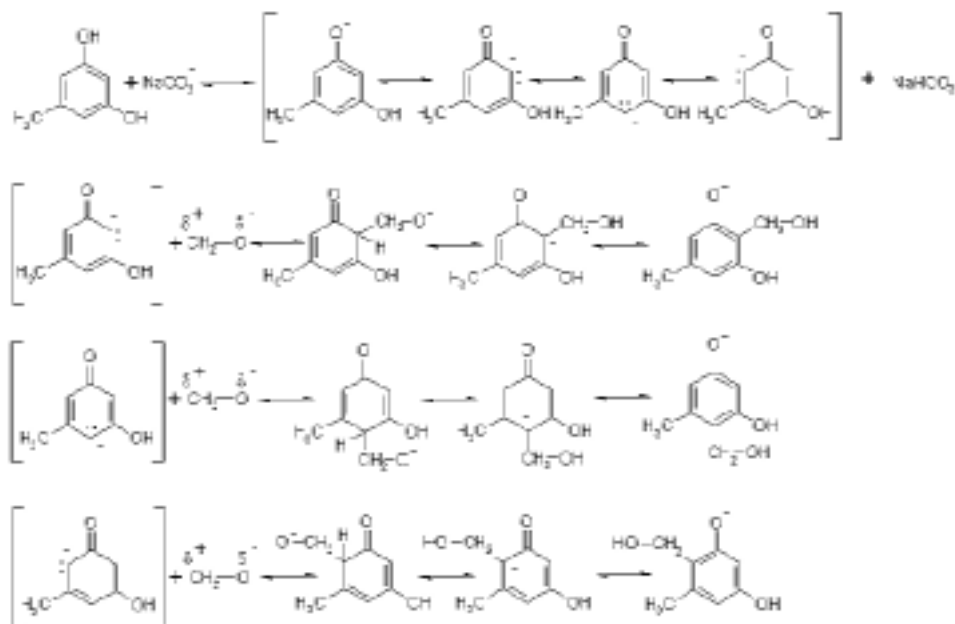


Figure 1 Reaction mechanism for the addition of formaldehyde on 5-methylresorcinol in basic medium

Addition of formaldehyde takes place in 2nd, 4th and 6th position due to the hydroxyl groups in 1st and 3rd position and methyl group in 5th position. This causes relatively fast gelation in comparison of phenol-formaldehyde gel, which has only one directing group.

Solutions No. 18, 19 and 20 contained less catalyst than other solutions and no gelation occurred at that temperature. Gel 22, where technical methylresorcinol (Honeyol™ with 59.6% content of MR) was used instead of pure did not gelate properly at these conditions.

Obtained gels were measured and radial shrinkage and densities were calculated. Results are shown on **figure 2** and **3**.

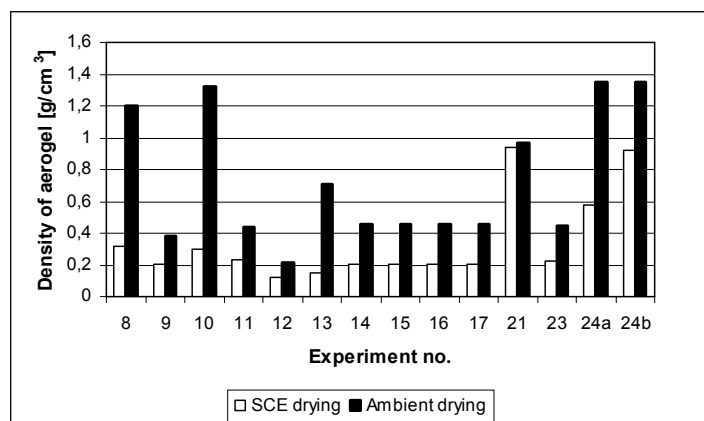


Figure 2 Densities of supercritically dried organic aerogels and aerogels dried at ambient conditions

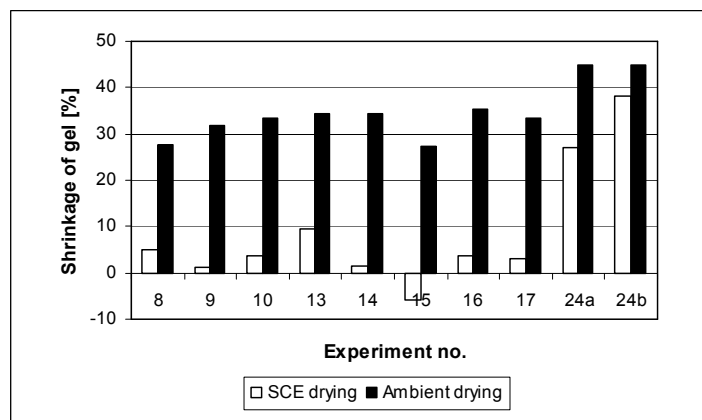


Figure 3 Shrinkage of supercritically dried organic aerogels and aerogels dried at ambient conditions compared to wet gel

Methylresorcinol-formaldehyde organic aerogels which did not gelate or gels were not bulk, are not included on **figure 3**.

As can be seen on both figures, supercritical drying results in lower densities and less shrinkage compared to drying in ambient conditions. Aerogels 8-17 on **figure 3** have densities between 0.2 and 0.3g/cm³ and shrinkages from 1 to 9%. Measurements of gel 15 prove negative shrinkage. Experiments have shown (gels 11, 12, 13) that more water in original solution leads to greater shrinkage during SC drying. All the gels obtained were beige and opaque in colour except gels 24a and 24b, where the amount of catalyst is greater (MR/C=16), gel particles are smaller and wet gel is red and transparent. Drying either way does not maintain the transparency of the gel. Gel is also thicker and shrinkage during SC drying is large compared to gels where less catalyst was used (MR/C=60). 4 hours longer supercritical extraction (24a) decreases shrinkage 11% and lowers the density more than 1.5 times. Using resorcinol as precursor, transparent gel is obtained at R/C ratios 25-400 [4].

Gel 21, formed in acidic medium, is inhomogeneous but there is no difference between aerogel made using SCE or ambient conditions for drying. Comparing gels 8 to 24b, the lowest density and minimum shrinkage has a gel with molar ratios MR/FA= 0.5, MR/C=60, W/MR=45.

Aerogels were analyzed using infrared spectrometry.

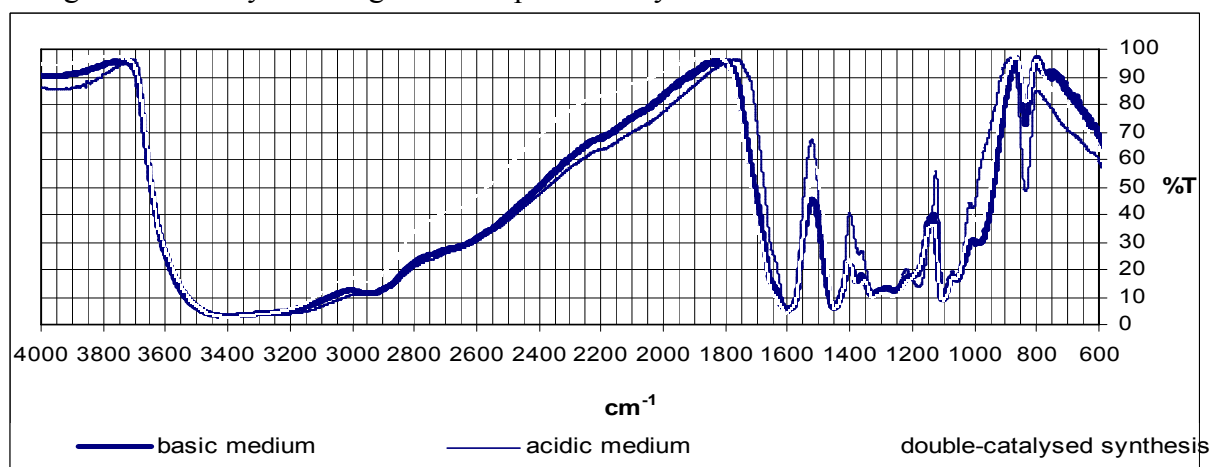


Figure 4 MR/FA aerogel (MR/FA=0.5, MR/C=60, W/MR=45) synthesized in basic, acidic and double-catalysed conditions.

At 1000, 1500 and 1400 cm^{-1} transparency ($T\%$) of IR is the smallest in basic conditions. In these regions IR light is absorbed by aromatic dialcohols. Acetic acid dissolves some of this monomer turning the colour of solution yellowish and making the gel more transparent for IR radiation. Number of methylene bridges ($-\text{CH}_2-$ area 2930 cm^{-1}) and ether bridges ($-\text{CH}_2-\text{O}-\text{CH}_2-$ area 1450 cm^{-1}) are almost equal in gels prepared in basic and in acidic medium. The spectrum describing double-catalysed synthesis does not show much advantage compared with one-step catalysis. Main difference is in region 830 cm^{-1} where IR absorption by 1-, 2-, 4-substituted benzene is greater in acidic than in basic conditions, although it was considered to be the other way around. SCE removes unpolymerized components from the gel - IR transparency has increased after SCE.

On **figure 5** are compared scanning electron microscope images of the same MR/FA gel samples dried in supercritical and ambient conditions. Pore sizes depend very much on the way of drying. SEM images make results of capillary forces visible. Shrinkage has caused cracking. Sizes of particles are also measurable – more catalyst leads to smaller particles.

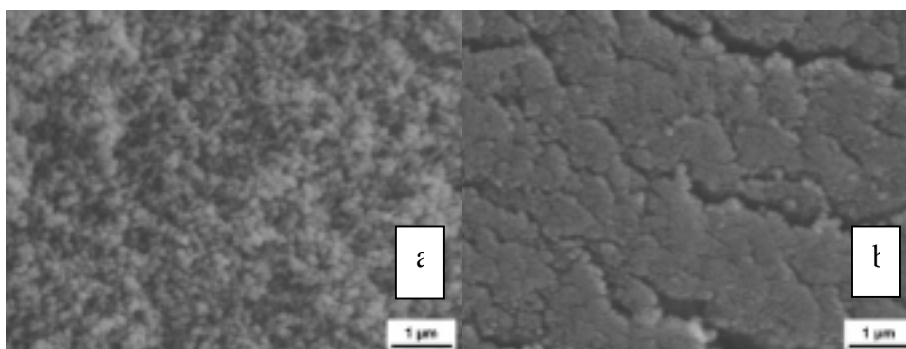


Figure 5 MR/FA organic aerogel (No.10 in **table 1**) dried supercritically (a) and under ambient conditions (b)

BET surface area measurements are carried out with supercritically dried gels 23, 14, 15, 16, 17 and ambient dried aerogel 15 (which is the same for gels 14, 16 and 17).

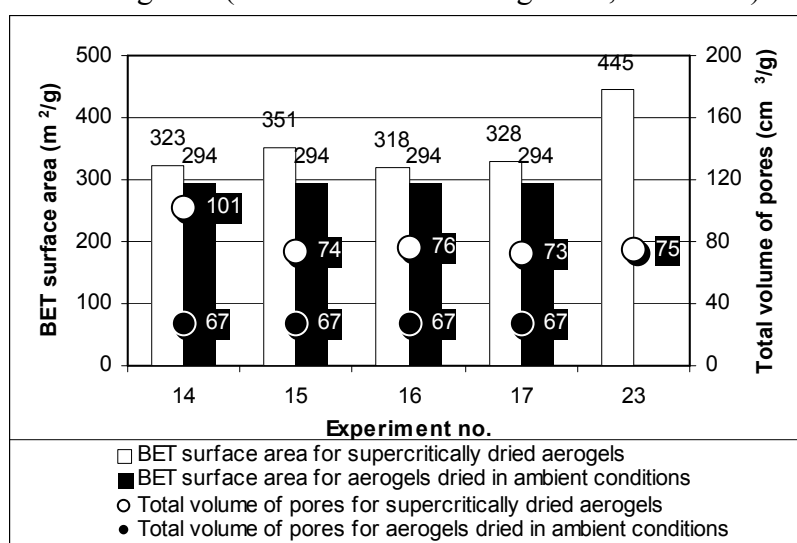


Figure 6 BET surface area and total volume of pores of aerogels depending on drying conditions

Aerogels 14, 15, 16 and 17 differ from each other by time of dynamic extraction of gel with liquid CO₂. For larger pore volume extraction should last at least 2.5 hours, BET surface area is less dependent of time. Gel 23 (R/FA aerogel) has a very large BET surface area despite the considerable shrinkage during SCE (shrinkage is comparable to gel 24b).

CONCLUSION

Methylresorcinol is appropriate precursor for preparing organic aerogels using basic or double-catalysed synthesis. Acidic medium gives no shrinkage using ambient drying but aerogel's homogeneity is unsatisfying. The minimum shrinkage and density are obtained using molar ratios MR/FA=0.5, MR/C=60 and W/MR=45. Extraction process takes altogether less than 3.5 hours for density 0.2g/cm³ and shrinkage 3%, when publications about R/FA organic aerogels give about 8 and more hours, still having large shrinkage. It is also rather easy to manipulate with pore and particle sizes of gel. To obtain gel from technical methylresorcinol, the preparation methods must be changed.

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