

PHYSICAL METHODS
OF INVESTIGATION

Methyltrimethoxysilane-Based Elastic Aerogels: Effects of the Supercritical Medium on Structure-Sensitive Properties

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Abstract—Effects caused by the type of solvent used for supercritical drying on the properties of methyltrimethoxysilane-based aerogels were studied. All of the aerogel samples studied were found to be hydrophobic and to efficiently adsorb nonpolar organic compounds.

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Aerogels are mesoporous solids having very low densities and heat conductivities and high specific surface areas and porosities [1]. Aerogels have widely been used as heat- or sound-insulating materials, adsorbents, heterogeneous catalysts, biomaterials, and in some other applications [2–6].

The preparation of aerogels comprises the steps of forming a gel by the sol–gel process, aging the gel, washing it from water and catalyst with the chosen solvent, and supercritical drying to remove the solvent at a temperature higher than the critical temperature of the solvent.

Alcohols and CO₂ are most commonly used as solvents for supercritical drying [7–10].

The main obstacle to the practical application of aerogels is their moisture sensitivity and low mechanical strength. Moisture resistance can frequently be enhanced through increasing hydrophobicity; for SiO₂ or Al₂O₃ aerogels, for example, an enhancement of moisture resistance can be provided by the trimethylsilylation of surface hydroxide groups [11, 12] or the fluorination of the surface using polyfluoroalkylsilanes as coprecursors together with tetraalkoxysilanes [13, 14]. Some researchers propose to use methyltrimethoxysilane CH₃Si(OCH₃)₃ (MTMS), which comprises a Si–C bond, as a precursor in the preparation of hydrophobic aerogels [15–17]. Aerogels prepared from MTMS combine hydrophobicity and elasticity with high specific surface areas and low densities. In addition, these aerogels are good sorbents for nonpo-

lar organic compounds [2] for use, for example, in oil spill decontamination.

Effects on the properties of aerogels caused by the solvent used for supercritical drying have poorly been studied. Meanwhile, our earlier results imply that the characteristics of the solvent are of primary importance for drying aerogels. For example, silica, alumina, or zirconia aerogels prepared by supercritical drying in ethers (diethyl ether or methyl *tert*-butyl ether) have specific surface areas about twice as high as the specific surface areas of aerogels dried in ethanol. Moreover, aerogels prepared in different solvents can also have different phase compositions. For example, a ZrO₂ aerogel prepared by drying in ethanol is crystalline and consists of a mixture of tetragonal and monoclinic ZrO₂ phases, whereas drying in ethers yields an amorphous aerogel [18].

When alcohols are used as supercritical solvents for preparing oxide aerogels, the aerogel surface can experience chemical modification to form alkoxy derivatives [7, 19–22]. The choice of alcohol affects the texture characteristics of the aerogel. So, silica, alumina, or zirconia aerogels dried in hexafluoroisopropanol have specific surface areas about twice as high as the specific surface areas of aerogels dried in ethanol [21].

We failed to retrieve data on how the choice of supercritical solvent would affect the properties of aerogels prepared from MTMS; meanwhile, this effect could be quite considerable. Therefore, our study was intended to elucidate the effect of the type of solvent used for supercritical drying on the properties of

Selected texture characteristics of MTMS-based aerogels

Sample no.	1	2	3	4	5	6	7	8
SC fluid	IP	Methanol	MTBE	CO ₂	EA	Hexane	Acetone	Air drying
S_{sp} , m ² /g	550 ± 30	50 ± 5	550 ± 40	550 ± 30	600 ± 40	600 ± 40	700 ± 50	650 ± 40
Wetting contact angle, θ , deg	140	138	134	130		141	–	–
Density, g/cm ³	0.15	0.17	0.15	–	–	–	–	0.13

MTMS-based aerogels. We have studied the texture and mechanical characteristics of our prepared aerogels and their interactions with water and organic solvents.

EXPERIMENTAL

Methyltrimethoxysilane (97%), isopropanol (IP, 99.5%+), methanol (99.9%), methyl *tert*-butyl ether (MTBE, 99%), ethyl acetate (EA, 99.6%), hexane (95%+), acetone (99.9%), HF (40% solution), and ammonium carbonate were used as received. All chemicals were purchased from Acros.

Specific surface areas of aerogels were determined by low-temperature nitrogen adsorption on an ATKh-6 analyzer (Katakona, Russia) using the six-point Brunauer–Emmett–Teller (BET) model. Prior to measurements, samples were flushed by a dry helium flow for 30 min at 200°C.

X-ray powder diffraction patterns of solid samples were recorded on a Rigaku D/MAX 2500 diffractometer (CuK α radiation) at a goniometer velocity of 2°/min.

Wetting contact angles were measured on an FTÅ200 instrument (First Ten Angstroms). Photographs were processed using FTÅ200 software.

Aerogel Preparation Procedure

Gel preparation. 0.955 g (0.007 mol) of MTMS was dissolved in 1.26 g (0.021 mol) of IP, then 40% aqueous HF (0.025 g (0.0005 mol) of HF) in 0.5 g (0.028 mol) of water) was added, and the mixture was stirred for 1 h. Afterwards, the mixture was added with 0.064 g (0.00067 mol) of ammonium carbonate dissolved in 0.6 g (0.034 mol) of water and then stirred for 1 min. The resulting sols (3–5 mL samples) were transferred into cylinder-shaped polypropylene containers. Gelation lasted 30–40 min. Then, gels were exposed to room temperature for 24 h, after which they were washed with the chosen solvent once a day during 5 days. The gels to be dried with supercritical hexane were first washed with isopropanol once a day during 3 days, then with hexane once a day during 3 days. The gels to be dried with supercritical CO₂ were washed with isopropanol.

Supercritical drying. A glass test-tube containing a gel under a solvent layer (16–18 mL) was placed in an autoclave ($V = 38$ mL). The autoclave was mounted inside a furnace and then heated at a rate of ~100 K/h to a temperature that was 15–25°C higher than the critical temperature of the solvent. The supercritical drying temperatures for isopropanol, methanol, methyl *tert*-butyl ether, ethyl acetate, hexane, and acetone were 250–260°C (the autoclave pressure was 6.0–7.0 MPa), 255–265°C (9.0–10.0 MPa), 240–250°C (5.0–6.0 MPa), 265–275°C (5.0–6.0 MPa), 250–260°C (4.0–5.0 MPa), and 250–260°C (6.0–7.0 MPa), respectively. Then, the pressure in the heated autoclave was gradually reduced to the atmospheric value, and the autoclave was evacuated for 30 min, cooled, and unsealed.

Supercritical drying in CO₂ was performed at 50°C and 15 MPa.

RESULTS AND DISCUSSION

We chose seven different solvents to study how the solvent used for supercritical drying can affect the properties of aerogels, namely: isopropanol, methanol, methyl *tert*-butyl ether, supercritical CO₂, ethyl acetate, hexane, and acetone. A solvent suitable for washing and supercritical drying should be capable of dissolving an excess water and residual monomers and oligomers (for this reason, we employed the procedure described in the EXPERIMENTAL for hexane, which is immiscible with water), and should also have acceptable values of critical parameters (T_{cr} and p_{cr}). The lowest possible values of critical parameters facilitate the hardware embodiment and reduce the cost of the supercritical drying process.

One of the isopropanol-washed gel samples was additionally air dried.

All of the aerogel samples prepared were X-ray amorphous as probed by X-ray powder diffraction.

The major texture characteristics of aerogel samples are compiled in the table.

One can infer from the table that the specific surface areas of MTMS-based aerogels are weakly affected by the type of solvent used for supercritical drying. An exception is methanol-dried samples, whose specific surface areas are about one tenth the specific surface areas of aerogels dried in other sol-

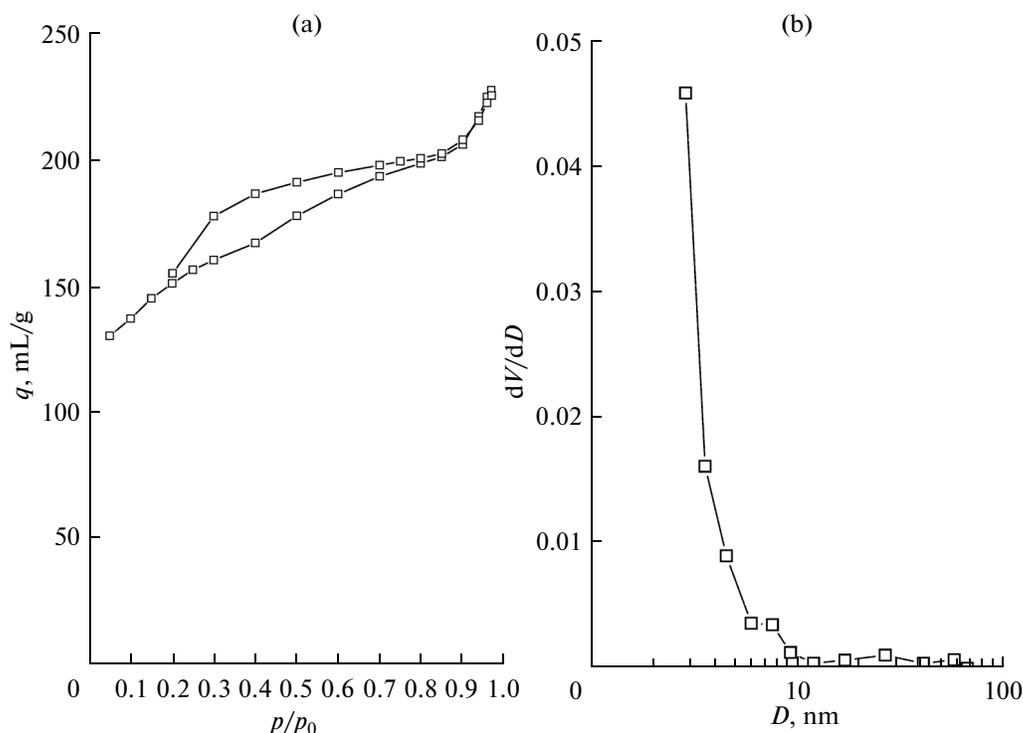


Fig. 1. (a) Complete sorption–desorption isotherm and (b) pore size distribution for an MTMS-based aerogel sample prepared by supercritical drying in isopropanol.

vents. We suppose that this ten-fold decrease in specific surface area can be explained by the high solubility of the gel in methanol and the associated enhancement of dissolution–reprecipitation of the gel framework and thickening of capillary walls. This supposition is confirmed by literature data that the solubility of silica gel heated in methanol is two orders of magnitude higher than its solubility in isopropanol [19]. There are no such data for MTMS-based polymers, but Ostwald ripening presumably can operate in this case, too.

Figure 1a displays the complete sorption–desorption isotherm for an MTMS-based aerogel dried in isopropanol (table, sample 1). This isotherm is close to type IV in the IUPAC classification and has a well-defined hysteresis in the region of relatively low partial pressures (~ 0.2 – 0.7). An analysis of the desorption branch of the complete sorption–desorption isotherm served us to plot a pore-size distribution diagram (Fig. 1b); this diagram indicates that only very small mesopores (< 10 nm) existed in the sample.

All of the prepared aerogels had high elasticity; a sample dried in methanol remained monolithic even under heavy strain (Fig. 2a). Aerogels dried in other solvents had lower elasticities and were destroyed when some ultimate strain (Fig. 2b).

The air drying of an isopropanol-washed sample gave intriguing results. The xerogel prepared in this

way also had a high specific surface area and did not lose elasticity (table, sample 8).

Our standpoint is that there are two reasons behind the relatively weak effect of the drying method on the properties of MTMS-based aerogels.

One suggested reason behind a high specific surface area is a high hydrophobicity of the sample. According to the Laplace equation (1) below, the capillary pressure that destroys the gel framework tends to zero as the wetting contact angle θ approaches 90° , thereby promoting removal of the solvent without destroying gel structure [23]:

$$P_c = -2\gamma(\cos\theta)/r, \quad (1)$$

where P_c is capillary pressure, γ is surface tension coefficient of the solvent, θ is wetting contact angle, and r is capillary radius.

The other reason behind the retention of high values of the specific surface area upon drying consists in the elasticity of gels. Capillaries are shrunk by capillary forces and then return to their initial condition, while the porosity and specific surface area of the sample change only insignificantly.

All of our synthesized aerogel samples indeed had high hydrophobicities; the water wetting contact angle values θ ranged between 130° and 141° and were only insignificantly affected by the solvent used for supercritical drying. In addition, they floated on water for several months without being destroyed, sank in hex-

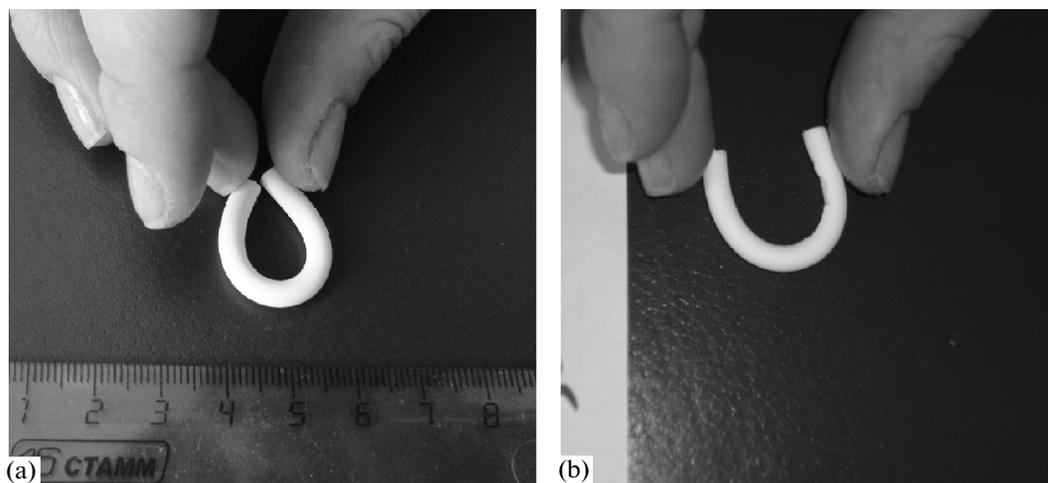


Fig. 2. Elasticity of MTMS-based aerogels dried in (a) methanol and (b) isopropanol.

ane (Fig. 3), and adsorbed considerable amounts of hexane from the water surface.

In summary, MTMS-based aerogels are a classic example illustrating the feasibility to prepare aerogels that would have high elasticity and resistance to mechanical impacts. Our results reported above imply that the texture characteristics (in particular, specific surface area) and elasticity of such the aerogels can depend on the solvent used for supercritical drying. For example, an aerogel sample dried in methanol has a

one order of magnitude lower specific surface area than in samples dried in any of the other tested solvents, while having high elasticity. Air-dried MTMS-based aerogels retain elasticity and high specific surface areas.

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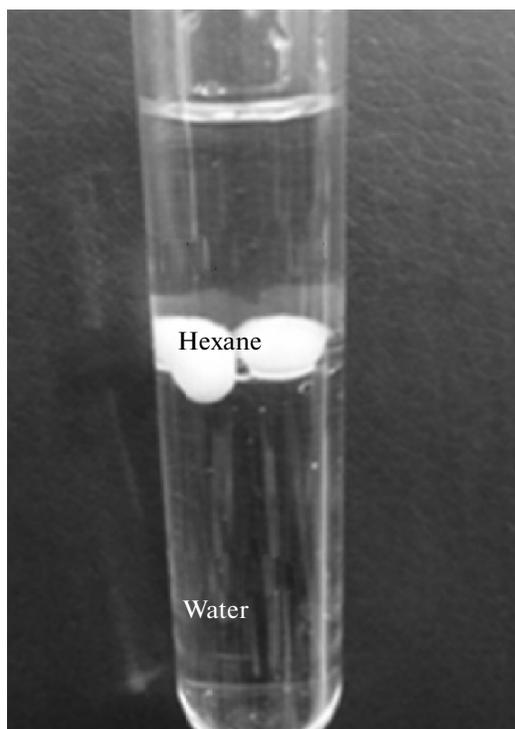


Fig. 3. Hydrophobic aerogel at the hexane/water interface.

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