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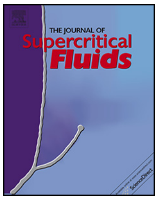

Hexafluoroisopropyl alcohol as a new solvent for aerogels preparation

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ABSTRACT

Fluorinated alcohols are claimed to be promising solvents for supercritical drying. A number of metal oxide aerogels (both monoliths and powders) including silica, alumina and zirconia were prepared using hexafluoroisopropyl alcohol. It is shown that the specific surface area of all the aerogels dried in hexafluoroisopropyl alcohol is twice that of the aerogels prepared in ethanol. Surface modification of aerogels with fluorinated organic species is shown to take place upon supercritical drying.

1. Introduction

Aerogels are mesoporous solid materials possessing unique properties including very low bulk density (up to 98% of their volume is air), large specific surface area and high thermal stability among others [1]. Since their discovery in 1931 [2], great efforts were made to develop industrial and domestic applications of aerogels. Nowadays they are used as reusable oil spills adsorbents [3], CO_2 scavengers [4,5] and water desalination materials [6]. A very large specific surface area makes aerogels promising catalysts and catalyst supports [7–10], energy storage materials [11–14] and hydrogen accumulators for fuel cells [15]. Preparation of graphene–aerogels electroconducting nanocomposites [14,16–18] presents a very promising recent area of application.

The most interesting feature of aerogels is their extremely low thermoconductivity up to $0.004\,W\,m^{-1}\,K^{-1}$ [10]. For instance, organic aerogels are used as thermoinsulators in space exploration technologies and in special clothing including sportswear [10]. Great efforts were made to develop the use of aerogels as thermoinsulating windows since high transparency and low thermoconductivity makes aerogels an ideal material for this application.

Aerogels are usually prepared by a sol–gel technique using supercritical drying (SCD) [1]. A solvent removal at a temperature exceeding its critical temperature is a necessary stage of this procedure. Thus the critical temperature of the solvent is a key parameter which determines the overall energy consumption in course of SCD as well as the resultant aerogels' properties. Alcohols and carbon dioxide (CO_2) are the most conventional types of SCD fluids for aerogels' preparation [19]. SCD with CO_2 is widely used since this compound is non-flammable and has a low critical temperature (31 °C). However, SCD with CO_2 requires expensive equipment. On the contrary, SCD in alcohol media is performed using comparatively low cost equipment, but alcohols are flammable substances, having a higher critical temperature.

Little is known about the influence of the nature of supercritical solvent on composition and structural characteristics of aerogels, including specific surface area and porosity. Only a few publications were found concerning the comparative study of the influence of the solvent used for supercritical drying on aerogels' properties

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[19–23]. The effects of different SC fluids (methanol, ethanol, 2-propanol and CO_2) on the properties of silica aerogels were reported [19]. It was found that the surface of samples prepared by SCD in alcohols contained corresponding alkyl groups, and the presence of these groups affected some aerogels' properties such as porosity and transparency. It is also believed that partial dissolution of gels in alcohols can occur [21], causing unexpected changes in aerogel microstructure and properties. It was shown that CO_2-dried and methanol-dried aerogels are substantially different in structure. That finding was attributed to the ripening of the aerogel network in methanol at high temperatures [22]. We have recently shown that the use of diethyl and methyl-*t*-butyl ethers instead of ethanol leads to a substantial increase in aerogels' specific surface area [23]. Isolated examples presented here confirm clearly that further study on the effects of the SCD media on the structure and properties of aerogels is needed.δ

We supposed that a non-flammable hexafluoroisopropyl alcohol (HFIP, $(CF_3)_2CHOH$) (T_{crit} = 189 °C, P_{crit} = 3.02 MPa) [24] could be a good alternative to ethanol (T_{crit} = 243 °C, P_{crit} = 6.38 MPa), methanol (T_{crit} = 239.4 °C, P_{crit} = 8.1 MPa) and isopropanol (T_{crit} = 235 °C, P_{crit} = 4.8 MPa) because of substantially lower critical parameters. Fluorinated alcohols (e.g. trifluoroethanol or HFIP) are much more acidic than their non-fluorinated analogs (HFIP pK_a (H_2O) 9.3; isopropanol pK_a (H_2O) ~17) [25] and thus could chemically modify the surface of aerogels. In addition, HFIP dissolves water and other polar substances and can remove them from hydrogel pores at the washing stage.

In this paper, we report on the first use of HFIP as a supercritical drying medium and describe a HFIP-assisted preparation of a number of oxide aerogels including silica, alumina and zirconia, all possessing a high specific surface area.

2. Materials and methods

2.1. Materials

Aluminum nitrate, $Al(NO_3)_3{\cdot}9H_2O$ (Acros, 99+%), propylene oxide (Aldrich, 99%), tetraethylorthosilicate ($Si(OEt)_4$) (Aldrich, 99%), zirconium *n*-propoxide ($Zr(OPr)_4$) (70 wt% in propanol, Aldrich), HF 40% aqueous solution, ethanol (Aldrich, ≥99.5%), HFIP (Aldrich, 99%) were used as received.

2.2. Preparation of gels

2.2.1. Preparation of sols

2.2.1.1. SiO_2 [26]. An amount of 5.6 g (0.027 mol) of $Si(OEt)_4$ and 4.8 mL (0.081 mol) of ethanol were mixed in a plastic beaker and cooled to 3–5 °C. 1.9 mL (0.108 mol) of deionized water and 0.054 mL of 40% HF (0.0012 mol) solution were mixed in another beaker and also cooled to 3–5 °C. The second solution was then added to the first solution and stirred for 1–2 min. The molar ratio $Si(OEt)_4$:EtOH:HF:H_2O = 1:3:0.05:4.

2.2.1.2. Al_2O_3 [27]. $Al(NO_3)_3{\cdot}9H_2O$ (4.6 g, 0.0123 mol) was dissolved in 20 mL (0.343 mol) of ethanol and then propylene oxide (7.83 g, 0.135 mol) was added to the resultant clear solution. The molar ratio $Al(NO_3)_3{\cdot}9H_2O$:EtOH:propylene oxide = 1:28:11. The reaction mixture was stirred for 5 min.

2.2.1.3. ZrO_2 [28]. Zirconium *n*-propoxide solution (3.25 mL) was dissolved in a mixture of 3 mL of *n*-propanol and 0.38 mL of HNO_3 (70%) and cooled to 3–5 °C. 0.262 mL of distilled water was mixed with 3 mL of *n*-propanol in another beaker and cooled to 3–5 °C. The water/alcohol mixture was then added to the alcoxide/acid/alcohol mixture and stirred for 10–20 s.

2.2.2. Gels preparation

Sols (3–5 mL) were poured into cylindrical polypropylene containers, sealed and left to gelate and age at room temperature for 24 h. The resultant gels were soaked in ethanol or HFIP for 24 h to exchange the pore liquid for the solvent chosen. This procedure was repeated five times. Then the gels formed were placed into an autoclave for supercritical drying.

2.3. Supercritical drying

Supercritical drying was performed as follows: a gel sample (3–5 mL) in a glass tube containing ~14–16 mL of an appropriate solvent was placed into a stainless steel autoclave (V = 38 mL). The autoclave was sealed and heated to a temperature exceeding the critical temperature of the solvent. The heating rate was approximately 100 °C/h. For ethanol and HFIP, the drying temperatures were 260–270 °C and 210–215 °C, respectively. The measured pressure in the autoclave at the beginning of the drying procedure reached 7.5–9.0 MPa and 4.5–5.0 MPa, respectively.

After reaching the desired temperature, the pressure was evenly decreased to atmospheric level during 2 h. Then the hot autoclave was evacuated in vacuum for 30 min, cooled to room temperature and opened.

2.4. Characterization of the aerogels

The specific surface area and porosity of the aerogels were determined by low-temperature nitrogen adsorption measurements with an ATX-06 analyzer. The specific surface area values were determined using a 5-point Brunauer, Emmett and Teller (BET) method at the relative pressure range of P/P_0 = 0.05–0.25; the correlation coefficient of the corresponding linear regressions in the coordinates of the BET equation was not less than 0.9975. Pore volume distributions were determined according to the Barrett, Joyner and Halenda (BJH) method, by the analysis of a desorption branch of an adsorption–desorption isotherm (28 points). Powder X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max 2500 diffractometer (CuKα radiation). Energy dispersive X-ray analysis (EDX) was performed using a field emission scanning electron microscope Carl Zeiss NVision 40 equipped with Oxford Instruments X-MAX analyzer operating at 20 kV accelerating voltage. Thermogravimetric and differential thermal (TGA/DTA) analysis of the samples was performed in air using a Pyris Diamond thermoanalyzer (Perkin–Elmer) in the temperature range of 20–800 °C (heating rate 10 °C/min). Solid state ^{19}F and ^{1}H NMR experiments were performed on a Bruker AvanceIII 400 spectrometer with $CFCl_3$ and TMS as external references. Larmor precession frequency was 376.5 MHz for ^{19}F and 400 MHz for ^{1}H. ^{19}F NMR spectra were recorded using 9 μs pulse length, accumulating 64 repetitions for each spectrum.

3. Results and discussion

We performed SCD of silica, alumina and zirconia gels in both HFIP and ethanol to reveal the influence of the SCD media on the properties of the resulting aerogels. Upon drying, all silica and alumina aerogels kept their monolithic appearance while zirconia samples were disintegrated into powders.

X-ray diffraction studies have shown that silica and alumina aerogels are completely amorphous. X-ray diffraction patterns of zirconia aerogels prepared by supercritical drying in HFIP also correspond to amorphous zirconia, and are identical to those typical to hydrous zirconia precipitated from aqueous solutions of inorganic zirconium salts [29]. A zirconia aerogel sample dried in ethanol is a mixture of two crystalline phases (see Fig. 1): tetragonal ZrO_2 (PDF 42-1164) and monoclinic ZrO_2 (PDF 37-1484). The volume