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Diethyl and methyl-*tert*-buthyl ethers as new solvents for aerogels preparation

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ABSTRACT

New solvents for aerogels synthesis by supercritical drying namely diethyl ether and methyl-*tert*-buthyl ether are proposed. A number of oxide aerogels including silica, alumina and zirconia were prepared using these solvents. Composition and properties of aerogel samples were studied using BET, XRD and TGA–DTA methods.

1. Introduction

Aerogels are mesoporous solid materials possessing unique properties including very low bulk density (up to 99% of their volume is air), large specific surface area, low thermal conductivity, high thermal stability, etc. [1]. Aerogels can be used as sorbents, support for heterogeneous catalysts, very light and effective thermal insulators, fillers, hydrogen fuel storage materials, etc.

Oxide aerogels are generally prepared by washing of hydrogels with appropriate solvents for water removal followed by drying under supercritical conditions (supercritical drying, SCD). Alcohols and carbon dioxide (CO_2) are the most conventional types of SCD fluids for aerogels preparation [2]. SCD with CO_2 is widely used since the latter is non-flammable and has a low critical temperature (31 °C). However, SCD using CO_2 requires expensive equipment. On the contrary, alcohols are flammable substances having a higher critical temperature (e.g. 243 °C for ethanol). SCD in alcohol media requires comparatively low cost equipment.

We could find only a few works concerning the comparative study of the influence of a solvent used for supercritical drying on aerogels properties [2–6]. The chemical interaction between gel and media is expected to be more pronounced upon alcohol SCD than upon CO_2 SCD. For example, partial dissolution of gels in alcohols can occur upon SCD [4,5]. This process can cause unexpected changes in aerogel microstructure and properties. Tajiri et al. reported the effects of the SC fluids (methanol, ethanol, 2-propanol and CO_2) on the properties of silica aerogels [2]. They found that the surface of samples prepared by SCD in alcohols contains corresponding alkyl groups. The presence of these groups influences some aerogels properties such as porosity and transparency. Small-angle X-ray and neutron scattering techniques were used to compare aerogels prepared by CO_2-assisted and methanol-assisted SCD. Differences in the structure of these aerogels were found which were attributed to ripening of the aerogel network during methanol-assisted SCD at high temperatures [6]. It is obvious that further study on the effects of the SCD media on aerogel properties and microstructures is required.

A solvent removal at a temperature exceeding the critical temperature of the media is a necessary stage of aerogel synthesis. So, the critical temperature of the solvent is a very important parameter which determines drying conditions. We supposed that diethyl (T_{crit}=193.4 °C, P_{crit}=3.61 MPa) and methyl-*tert*-butyl (T_{crit}=224.1 °C, P_{crit}=3.44 MPa) ethers could be good alternatives to ethanol (T_{crit}=243 °C, P_{crit}=6.38 MPa) and methanol (T_{crit}=239.4 °C, P_{crit}=8.1 MPa). In addition, dry ethers dissolve water and can effectively remove water from hydrogel pores at the washing stage.

In this paper, we report the first use of diethyl and methyl-*tert*-butyl ethers as supercritical drying media. A number of oxide

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aerogels including silica, alumina and zirconia were obtained for the first time using these SC fluids.

2. Experimental

Materials: Aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$, 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%), diethyl ether and methyl-*tert*-butyl ether (Aldrich, 99%) were used as received.

Preparation of gels: All gels were synthesized using a sol–gel technique.

Sols preparation—SiO_2 [7]: 6 mL (0.027 mmol) of $Si(OEt)_4$ and 4.7 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 g of 40% HF solution were mixed in another plastic beaker and also cooled to 3–5 °C. The second solution was then added to the first solution in one portion and stirred for 1–2 min.

Al_2O_3 [8]: $Al(NO_3)_3 \cdot 9H_2O$ (4.6 g, 0.0123 mol) was dissolved in 20 mL of ethanol and then propylene oxide (7.83 g, 0.135 mol) was added to a clear solution. The reaction mixture was stirred for 5 min.

ZrO_2 [9]: 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 and cooled to 3–5 °C. 0.262 mL of distilled water was mixed with 3 mL of *n*-propanol in a separate beaker and cooled to 3–5 °C. The water/alcohol mixture was added to the alkoxide/acid/alcohol mixture and stirred for 10–20 s.

Gels preparation: Sols prepared by the methods described above were poured into cylindrical polypropylene containers, sealed and left to gelate at room temperature for 24 h. Resulting hydrogels were soaked in ethanol, diethyl or methyl-*tert*-butyl ethers for 24 h to exchange the pore liquid for the solvent chosen. This procedure was repeated for 5 times. Then the gels formed were placed into an autoclave for supercritical drying.

Methods: Supercritical drying was performed as follows. Gel sample in a glass tube containing ~14–16 mL of an appropriate solvent was placed into a stainless steel autoclave (V~40 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, diethyl ether, and methyl-*tert*-buthyl ether the drying temperatures were 260–270 °C (the measured pressure in the autoclave at the beginning of the drying procedure reached 7.5–9.0 MPa), 210–220 °C (5.0–6.0 MPa) and 240–250 °C (4.5–5.0 MPa), respectively. After reaching the desired temperature, the valve was opened; the pressure was evenly decreased to atmospheric in 2 h. Then the hot autoclave was evacuated in vacuum for 30 min, cooled to room temperature and opened.

The specific surface area of the aerogels was determined by low-temperature nitrogen adsorption measurements with an ATX-06 analyzer by an 8-point BET method. Experimental values were plotted against P/Po according to the Brunauer, Emmett and Teller (BET) equation; the correlation coefficient, *r*, of the linear regression was not less than 0.9975. Powder X-ray diffraction (XRD) analysis was carried out on a Rigaku D/Max 2500 diffractometer ($Cu_{K\alpha}$ radiation). Thermogravimetric and differential thermal (TGA/DTA) analysis of the samples was performed in air using Pyris Diamond thermoanalyzer (Perkin-Elmer) in the temperature range 20–1100 °C (heating rate 10 °C/min). Microstructure of ;the samples was studied using Carl Zeiss NVision 40 scanning electron microscope (micrographs were obtained at 7 kV acceleration voltage). Before analysis samples were coated with Au/Pd 3 nm layer.

Table 1
The surface area of aerogels, m^2/g.

Aerogel	Solvent		
	Ethanol	Diethyl ether	Methyl-*tert*-butyl ether
SiO_2	460 ± 60	880 ± 80	980 ± 80
Al_2O_3	430 ± 65	700 ± 105	760 ± 110
ZrO_2	250 ± 37	490 ± 60	400 ± 60

3. Results and discussion

Physical properties of aerogels: The surface area values (m^2/g) of aerogel samples are presented in Table 1. It is clearly seen that all aerogels dried in both ethers have approximately two times larger specific surface area compared to the samples dried in ethanol. Adsorption–desorption isotherms presented in Fig. 1 clearly show that absolute adsorption values for aerogels dried in ethers are significantly higher than for the ones dried in ethanol. Fig. 1 also reveals that the porosity of aerogels prepared using both ethers is higher than the porosity of ethanol dried ones. Adsorption–desorption isotherms are of type IV, i.e. samples are mesoporous materials containing interparticle pores. The hysteresis loops correspond to H3 type, probably due to the presence of slit-like interparticle pores [10,11].

SEM images (Fig. 2) reveal no distinct differences in the microstructure of samples prepared using different solvents.

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 diethyl and methyl-*tert*-butyl ethers also correspond to amorphous zirconia and are identical to those typical to hydrous zirconia precipitated from aqueous solutions of inorganic zirconium salts [12]. Zirconia aerogel

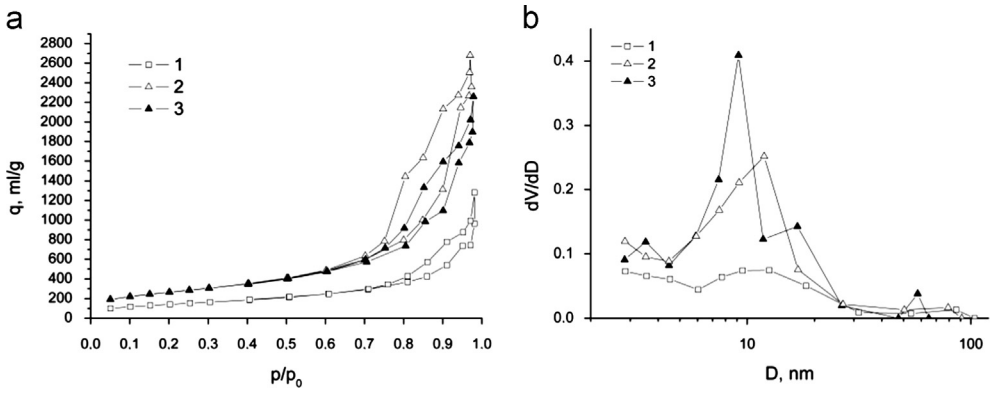

Fig. 1. (a) Sorption–desorption isotherms and (b) pore size distributions for SiO_2 aerogels prepared by supercritical drying in ethanol (1), methyl-*tert*-buthyl ether (2) and diethyl ether (3).