INFLUENCE OF SURFACTANTS ON SiO_2 AEROGELS

TORRES R. Jorge[1], CASAS-LUNA Mariano[1], TKACHENKO Serhii[1], KAISER Jozef[1]

[1]*Central European Institute of Technology, Brno University of Technology, Brno, Czech Republic, EU*
JorgeAlberto.TorresRodriguez@ceitec.vutbr.cz

Abstract

Silica aerogels, as well as those consisting of other metal oxides (alumina, zirconia, titania or mixture of these oxides), are extremely porous (up to 99%) high-tech materials with very high specific surface areas (≈1000 $m^2\ g^{-1}$) and low thermal conductivity (below 0.02 W / mK). The typical aerogel production process includes several steps and starts with the preparation of a sol. The next step includes a casting of the sol to obtain the required gel form via sol - gel transition and its drying in a supercritical drying chamber at supercritical conditions of CO_2 to obtain the desired product. Hence, it is of critical importance to determine how processing parameters (type of solvent, catalyst, surfactant, a medium of drying, temperature, pressure, the presence of rheological agents (RA)) influence the microstructure, morphology, transparency and other properties of the obtained aerogels.

In this work, we studied the effect on three synthesized systems: SiO_2-Triton, SiO_2-PVP and SiO_2-F127 using TMOS, MeOH-NH_4OH-H_2O at constant molar ratios of reactants 1:7:0.7:2.7, respectively. Chemical, structural and morphological results were performed by using FTIR and SEM techniques. SEM imaging analysis demonstrated a change in agglomerate size distribution (5-10 nm) depending on the system. Furthermore, the increase in the amount of F217 agent increased both the density, measured by sample dimensions, of produced SiO_2-F127 aerogels from 0.09 to 0.2 $g\cdot cm^{-3}$ along with the pore size.

Keywords: Aerogel, supercritical drying, surfactant, porosity

1. INTRODUCTION

Silica aerogels are materials that have high specific surface area, high porosity (up to 99%), small pore size (50 nm), low thermal conductivity (0.02 W / mK), and low refraction index [1]. Because of these unique properties, aerogels have been extensively studied not only for use as thermal insulators, but also as inter-metal dielectric materials, applications in optical and acoustic fields, and in the space industry [2, 3]. Additional applications of aerogels are found in battery electrodes, catalysts and electronic devices. As for thermal insulation application, generally monolithic SiO_2 aerogels provide a very low thermal conductivity due to its extremely high porosity and its three-dimensional interconnected microstructure. The thermal conductivity of aerogels is smaller than that of commonly used thermal insulator such as polystyrene foam, perlite, cork, metallic foams etc [4].

Silica aerogels are typically prepared by supercritical drying (SCD) of sol-gel derived wet gels to remove solvent while keeping the pore structure in the final product material [5]. Materials obtained by this methodology present good properties, nevertheless, the need to develop new methodological approaches allowing to obtain aerogels with improved characteristics, such as lower thermal conductivity, lower density, and higher transparency, is of current importance. In this context, it is of great interest to determine how processing parameters influence the microstructure, textural properties, thermal conductivity and other properties of the obtained aerogels.

Recent observations suggest that the textural properties (surface area, pore size, and pore volume) of silica porous materials can be improved by the addition of organic polymers that modifies the behavior of the colloidal particles and, therefore, leads to a change in physical properties [6, 7, 8]. In the present work, we studied the effect of three different organic water-soluble surfactants, such as Pluronic F127, Polyvinylpyrrolidone, and Triton X100, on the microstructure, pore morphology, chemical composition and density of the obtained surfactant templated SiO_2 aerogels.

2. EXPERIMENTAL DETAILS

2.1. Preparation of silica aerogels

The preparation of silica aerogels using the sol-gel process has been performed in accordance with the procedures previously described in the literature [3]. The chemicals used were tetramethyl orthosilicate (TMOS) $Si\text{-}(OCH_3O)_4$ (Sigma-Aldrich) as Si precursor, anhydrous 99.8% methanol (MeOH) CH_3OH (Sigma-Aldrich) as solvent, 30% ammonium hydroxide (NH_4OH) (Sigma-Aldrich) as catalyst, and distilled water, while polyvinylpyrrolidone (PVP), Triton-X100 (Sigma-Aldrich) and Pluronic F127 (Sigma-Aldrich) were utilized as modification agents.

The silica-surfactant composite aerogels were synthesized through hydrolysis and condensation of TMOS in the presence of the desired methanolic-surfactant solution of different concentrations. During a typical synthesis, TMOS was initially mixed with half of the amount of MeOH and stirred for 10 min; then this solution was mixed with a second solution containing the additional solvent and the required amount of template and stirred for 1h. Finally, an aqueous basic solution (NH_4OH / H_2O) was added to the resultant solution with continuous stirring for 15 minutes in order to obtain a homogeneous system. Then the resultant sols were transferred into a cylindrical beaker until gelation occurs. The silica-templated aerogels were aged in methanol for 36 h. All the gels were prepared with the molar ratio of $TMOS:MeOH:H_2O:NH_4OH = 1:7:0.01:4$, so the only variable was the type of the surfactants and the concentration of F127 in the ratio TMOS/F127 in the range of 0.0125 - 2. The samples obtained using such surfactants were named as S-F127, S-PVP, S-Triton, respectively, while that synthesized without surfactant was called A-SiO_2.

To finalize the preparation of aerogels, the solvent was removed by supercritical drying into an autoclave using CO_2 as a supercritical fluid. Two samples at the same time were placed into the main chamber, then filled with fresh methanol to avoid evaporation and cracking, and finally, the system was filled with liquid CO_2 up to a pressure of 5.1 MPa. Consequently, the system was heated up to 40 °C and a pressure of 8.2 MPa to ensure being above the critical temperature and the pressure of CO_2. The autoclave was maintained under these conditions for 1 h and then slowly depressurized up to the ambient pressure.

2.2. Microstructural and chemical characterization

The apparent density of the modified samples with F127 was calculated as a simple mass-to-volume ratio of the obtained sample. The chemical bonding of the pure surfactants and the composite aerogels were determined using Fourier Transform Infrared Spectroscopy (FTIR), (Spectrum 65 FTIR spectrometer, Perkin Elmer). To perform this analysis, silica aerogel was initially pulverized into a refined powder, mixed with Potassium Bromide (KBr), and pressed to form a sample pellet for FTIR measurements. Microstructure examinations of aerogel samples were carried out by scanning electron microscopy (SEM, High vacuum SEM JSM-7800F, JEOL). The agglomerate size distribution (ASD) was calculated by imaging analysis, measuring 400 agglomerates for each of the synthesized aerogels.

3. RESULTS AND DISCUSSION

To investigate the effect of the surfactant on the textural properties of the silica aerogels, different experiments were carried out in both absence and presence of the various surfactants Pluronic F127, Polyvinylpyrrolidone (PVP) and Triton X100. Visual observation of the obtained aerogel samples revealed that the pure A-SiO_2 sample was transparent and slightly cracked, S-F127 and S-Triton samples were almost similar with slightly opaque appearance, while S-PVP sample was of deep white color. **Figure 1** shows the surface morphology of the TMOS-based silica aerogels, where the different porous microstructure of the silica aerogels could be clearly visible. **Figure 1(a)** indicates that the A-SiO_2 aerogel has a three-dimensional structure made of dense and agglomerated sphere-like nanoparticles (d = 3 - 5 nm), producing agglomerates of around of 100 nm. An obvious increase in the macropore region can be noted in the aerogel S-PVP **Figure 1(b)** from few nanometers to around 1 μm, which can be due to the presence of PVP that separates the molecular species and retards the process of cross-linkage of siloxane chains [9]. This results in the increase of pore size are due to less contact between the neighboring particles. As a number of surfactant increases, the connectivity between the particles decreases with the decrease of their number.

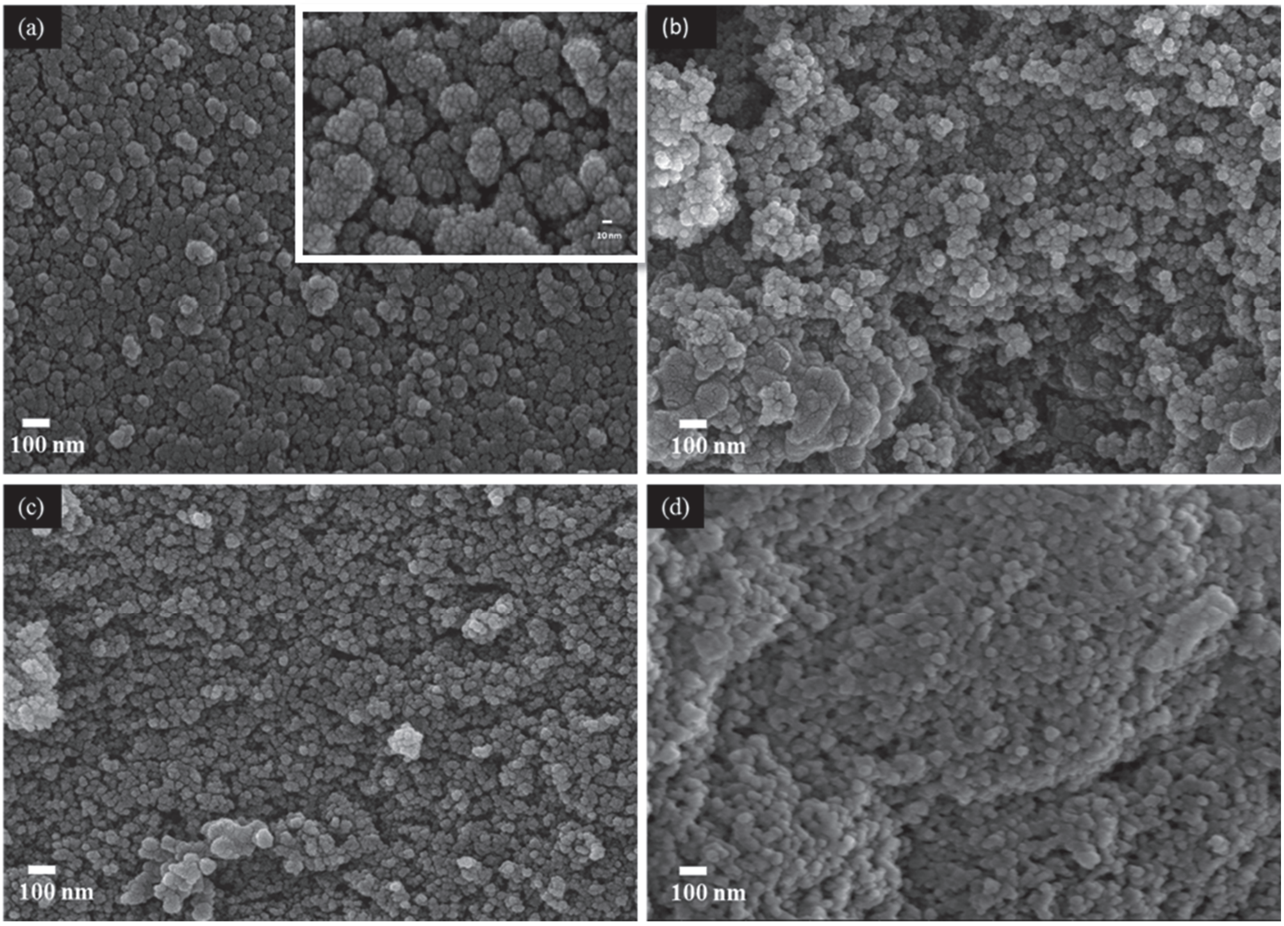

Figure 1 SEM surface morphology of modified nanoporous silica aerogels: (a) A-SiO_2, (b) S-PVP, (c) S-Triton, and (d) S-F127

Although to a lesser degree, the same effect can be observed in the sample containing Triton as a surfactant (**Figure 1**(c)), where the interconnected particles seemed to be less compacted, leading the formation of smaller agglomerates. In the case of the system S-F127, see **Figure 1**(d), the result is rather adverse, since the surfactant promotes the junctions between the particles, closing their porosity and leading to the apparent increase in particle size. The effect in the agglomerate size distribution is shown in **Figure 2**. Such modification of the ASD is due to a change in the surface energy promoted for the surfactant over the SiO_2 particles, this effect is more visible in the S-F127 sample due to the molecules of F127 are increasing the surface tension and making the SiO_2 particles unstable and charged with higher energy compared to pure SiO_2 aerogel and because of this, the colloidal system tends to decrease such energy by joining one other to increase the surface area and to have the least possible energy.

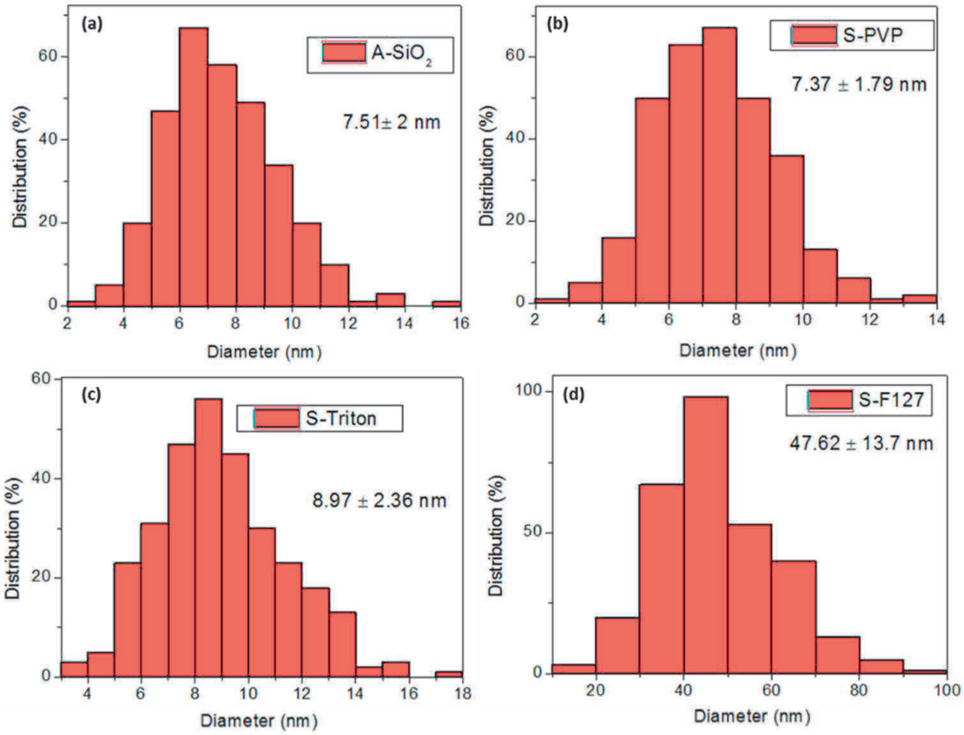

Figure 2 Agglomerate size distribution of the aerogels: (a) A-SiO$_2$, (b) S-PVP, (c) S-Triton, and (d) S-F127

The FTIR spectra patterns show the presence of the different surfactants (**Figure 3**). It is important to note that they show typical vibration bands of siliceous materials, such as the wide band situated around 3400-3450 cm^{-1} to correspond to the overlapping of the O - H stretching bands of hydrogen-bonded water molecules (H - O - H ···H), and SiO - H stretching of surface silanols hydrogen-bonded to molecular water (SiO-H···H$_2$O) [9]. Furthermore, the Si - O in-plane stretching vibrations of the silanol Si - OH groups appear at around 950 cm^{-1} [10], and the absorption bands corresponding to the adsorbed water molecules deformation vibrations appear at 1630-1650 cm^{-1} [11]. The adsorption of water molecules on the surface of the aerogels is due to the existence of surface silanol groups, and therefore due to the hydrophilic nature of these silica materials. The intense silicon-oxygen covalent bonds vibrations appear mainly in the 1000-1200 cm^{-1} range, revealing the existence of a silica network with asymmetric stretching vibrations of Si - O - Si[12]. Another band appearing at 814 cm^{-1} is due to the symmetric stretching vibrations of the bond Si - O - Si [13], and its bending mode appears at 460 cm^{-1} [14]. The low energy band at 565 cm^{-1} is assigned to Si - O stretching of the SiO$_2$ network effects[15]. The use of organic surfactants leads the formation of

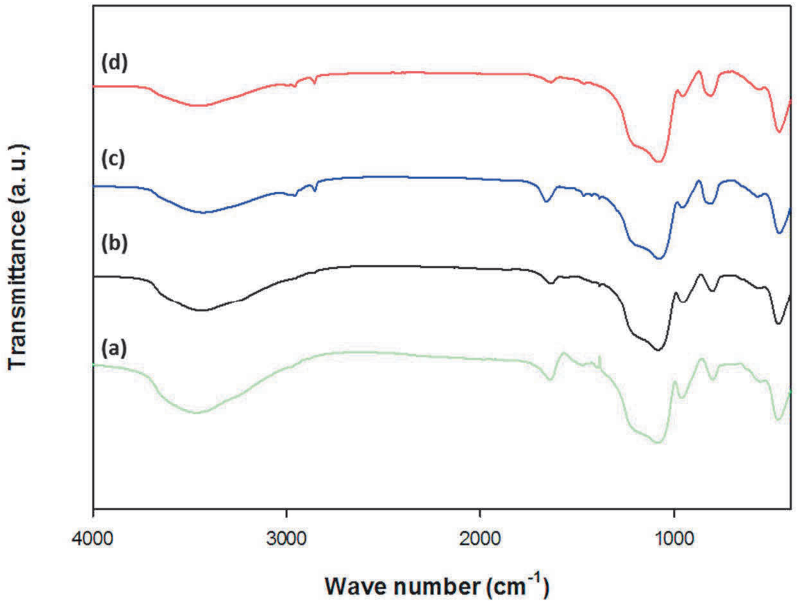

Figure 3 FTIR spectra of the silica aerogels: (a) A-SiO$_2$, (b) S-Triton, (c) S-F127, (d) S-PVP

surface methyl groups. The corresponding surfactant templated samples, show several peaks in the 2850-2950 cm^{-1} range assigned to the C - H symmetric and antisymmetric stretching vibrations of - CH_3 and - CH_2 groups also visible C - H symmetric and antisymmetric vibrations at 1385 cm^{-1} and 1415 cm^{-1} respectively [16].

The results of measured density are shown in **Figure 4**. It is obvious that incorporation of the surfactant into the SiO_2 matrix promotes an increase in aerogel apparent density. As it was expected, the increase of the density resulted not only from the incorporation of the surfactants but also from the enclosed structure that is formed in the case of F127 aerogel. It is important to remark that during the supercritical drying procedure the surfactant was not completely removed due to the high-pressure extraction process, and some residue of it stills presents in the final aerogel, which is clear from the increase in the apparent density and the detected C - H bonds by FTIR. Therefore, is necessary to heat up the final aerogel samples up to 400 °C and thus, ensure to remove the organic compounds from the SiO_2 matrix.

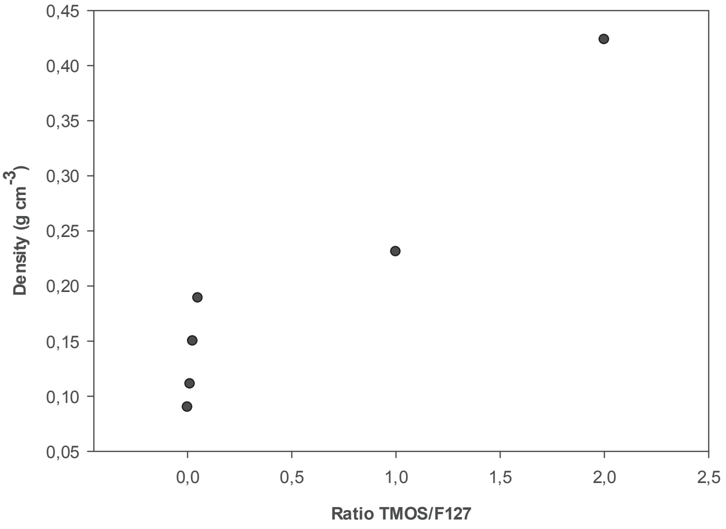

Figure 4 Apparent density of the system S-F127 varying the molar ratio TMOS/F127 from 1 to 2

4. CONCLUSION

In the present paper, we studied the effect on the textural properties of three different surfactants in the silica aerogels synthesized by sol-gel methodology. The modifier surfactant had strong effects on the physical properties of the system with a variation of the agglomerate size distribution with a possible effect on the surface tension, and transparency which is an indicative of a modification of the pore size. The presence of used organic compounds was detected by FTIR, and in a further work is necessary to investigate the removal of the surfactant by a thermal heating and get SiO_2 completely pure SiO_2 aerogels.

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