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Silica Aerogels by Supercritical Extraction

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Abstract

Aerogels of different densities were prepared from silica gels by supercritical drying in a high temperature and high pressure plant. Gels were synthesised from tetramethoxysilane (TMOS) using acetone or methanol as solvents. For the acetone gels, several volume ratios of precursor and solvent were used. Properties of the obtained aerogels were analysed and their pore structure was studied by gas/vapour adsorption and scanning electron microscopy (SEM). Changing the volume ratio of precursor and solvent reveals itself as an easy way to modify the density, porosity and mechanical strength of the acetone aerogels. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Aerogels are extremely porous materials, with porosities close to 90%. This characteristic provides the aerogels with some unique properties for a solid material. Although known since the thirties the synthesis method was much improved by Teichner *et al.*[1,2] in the late sixties opening the possibility to a much wider use of these materials. They are the lightest solids known, with densities as low as three times the density of the air. Due to their open porous network and their large surface area they are being investigated as support for catalysts. On the other hand, their very low thermal conductivity, even less than that of air, makes them ideal thermal insulators. Moreover, as aerogels can be made in general transparent, they are being used as superinsulators in windows and covers on solar thermal energy systems. Other applications are in Cerenkov radiation detectors, space crafts, insect killers, gelifiers, tooth paste, etc.

In this paper, different synthesis procedures of silica aerogels were tested searching for an easy route suitable for specific industrial applications. From different combinations of solvent (methanol and acetone) and catalyst (none, potassium hydroxide and ammonium hydroxide) two one-step routes were selected because of the quality and reproducibility of the resulting products.

Both syntheses routes use tetramethoxysilane (TMOS) as precursor. The first one consists of methanol as solvent and ammonium hydroxide (NH_4OH) as catalyst. In the second one no catalyst is added, acetone being the solvent. In this case different concentrations of solvent were used.

Several physical characteristics, mainly referred to the pore network, were studied in order to relate the aerogel properties with the synthesis process, allowing the synthesis of aerogels with selected properties for specific applications.

2 Synthesis of gels and supercritical drying

The reactives used were: a precursor (TMOS), a solvent, water and, eventually, a catalyst. For methanol gels the molar ratio of reactives were TMOS:methanol:water:catalyst (NH_4OH) = 1:12·25:4:6.5×10^{-2}.[3] For acetone gels, TMOS:acetone:water = 1:x:4, with four different values of x.[4] These values are listed in Table 1 together with v, where $v = \text{volume}_{\text{TMOS}}/\text{volume}_{(\text{TMOS}+\text{solvent})}$; this ratio identifies the four acetone syntheses (acetone-0·1, acetone-0·2, acetone-0·3 and acetone-0·4).

The following steps were common to both routes. A solution was firstly prepared by adding the solvent to TMOS drop-wise while stirring, after 5 min the water was added, eventually containing the catalyst. After stirring for 15 additional min, the solution was distributed in glass test tubes. The tubes were tightly closed and kept at room temperature until gelification took place, then the gels were covered with their respective solvents and left to age until supercritical drying. Gelation time

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Table 1. Solvent content in the gel preparation and gelation times

Label	*Solvent*	*Solvent amount (per mol of TMOS)*	$v_{(TMOS)}/v_{(TMOS+solvent)}$	*Gelation time*
Methanol	Methanol	12·25	0·08	3–7 min
Acetone-0·1	Acetone	1·224	0·10	57–114 days
Acetone-0·2	Acetone	0·544	0·20	10–13 days
Acetone-0·3	Acetone	0·317	0·30	6–8 days
Acetone-0·4	Acetone	0·204	0·40	2–3 days

Table 2. Aerogel shrinkage with respect to the gel precursor, aerogel density, surface area (± 10%) and volume porosity. The numbers within brackets indicates the error of the last digit

Label	$\Delta L/L_{gel}$	$\Delta V/V_{gel}$	*Density* ($g\,cm^{-3}$)	*Surface area* ($m^2 g^{-1}$)	*Porosity in volume*
Methanol	0·07(1)	0·27(1)	0·13(1)	470	0·94
Acetone-0·1	0·14(2)	0·43(3)	0·07(1)	420	0·96
Acetone-0·2	0·14(3)	0·42(3)	0·15(1)	550	0·93
Acetone-0·3	0·18(1)	0·47(3)	0·25(1)	466	0·89
Acetone-0·4	0·18(1)	0·46(3)	0·27(4)	589	0·88

depends strongly on the initial conditions, it ranges from a few minutes for methanol gels to months for the lower concentrations of precursor in acetone gels. A list of gelation times is provided in Table 1.

Supercritical extraction took place in a high temperature and high pressure plant.[5,6] Gels achieved the supercritical region of the solvent by pressurisation with CO_2 gas followed by slow heating to avoid thermal shock. In the supercritical region the liquid phase of the gel becomes a supercritical fluid. Once the liquid phase of the gel became a supercritical fluid the gas–liquid interface in the gel pores disappears. The fluid is then removed by slow evacuation,[7] although some shrinkage is unavoidable due to capillary process. The process finishes by cooling the samples till room temperature. As an example, Fig. 1 shows a supercritical drying cycle for the methanol aerogels.

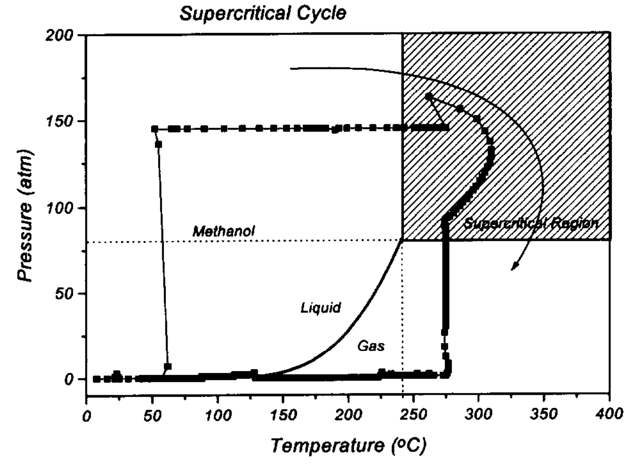

Fig. 1. Phase diagram and a supercritical drying cycle of a methanol gel. The methanol liquid–gas interface curve has been included. Every point of the graph correspond to an elapsed time of 5 min.

3 Characterisation and discussion

Aerogels obtained by both syntheses routes presented noticeable differences in their colour. Methanol aerogels were very transparent, with a slight blue shading. Meanwhile acetone aerogels had a white shading, their opacity decreases with the TMOS content. Aerogels were monolithic, without cracks. Acetone-0·1 aerogels were specially fragile.

Aerogel and gel dimensions were compared in order to measure the shrinkage produced during supercritical extraction. Results are presented in Table 2. Volume shrinkage for all acetone aerogels is about 45%, independently of the reactive concentrations. This shrinkage is clearly higher than that observed for methanol aerogels.

Densities of the obtained aerogels were calculated by dividing the aerogel mass by its measured volume. Volume porosity was calculated from the densities of the aerogel and the bulk material, $\rho_{(SiO2)} = 2{\cdot}19\ g\ cm^{-3}$.

Methanol aerogels present densities and porosities similar to those for acetone-0·2 (Table 2). For acetone aerogels, it has been observed that density increases, and porosity is reduced, when increasing TMOS content (Fig. 2), the variation could be adjusted to a straight line. Disregarding the effect of shrinkage, this is the behaviour one should expect, denser material need more precursor, leading to reduced porositites.

Powdered aerogels were used for X-ray diffraction experiments. Patterns consisted on a broad single peak centred at $2\theta = 23°$ (CuK_α radiation) revealing the amorphous nature of the aerogel structure.

The specific surface area was measured by gas/vapour adsorption technique using the Burnauer–Emmett–Teller (BET) analysis.[8] BET is actually a standard approach for analysing

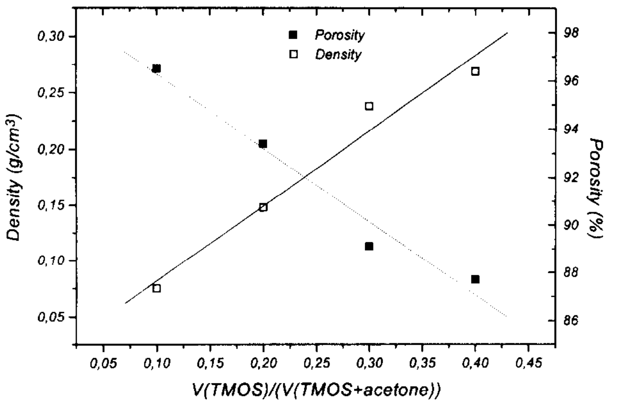

Fig. 2. Density and porosity for the different aerogels obtained from acetone gels.

nitrogen adsorption data at 77 K to determine the specific surface area. The analysis was performed using an equipment from Micromeritics Instrument Corp. The total surface area was similar for all the studied aerogels.

Scanning electron microscopy (SEM) is an efficient technique for comparing the pore structure of aerogels.[9] The aerogels were covered with an ultrathin gold layer to optimise the sample conductivity. Pores appear as darker areas in the SEM micrographs. Comparison of SEM micrographs of acetone and methanol aerogels [Fig. 3(a)(b)] reveals a narrower distribution of the pore size for the methanol aerogels.

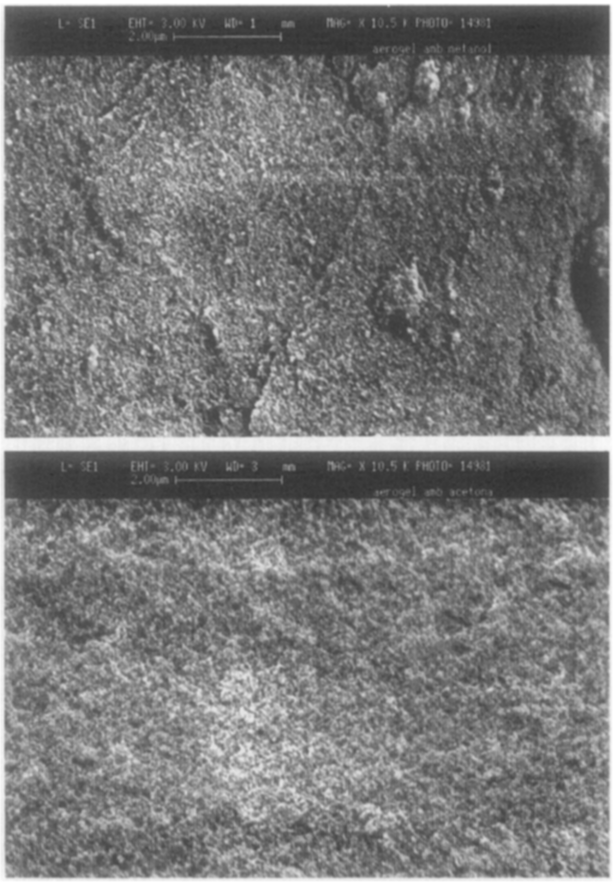

Fig. 3. SEM micrograph of aerogels obtained using different solvents: (a) methanol, (b) acetone.

4 Conclusions

TMOS concentration in acetone gels proves to be an easy way for controlling density and porosity of the resulting aerogels. During gel formation[10] hydrolysed TMOS forms the silica gel network and the solvent fills the gel pores. Increasing TMOS concentration in the starting solution, more silica skeleton is formed and then the aerogel will be heavier and its density larger.

BET analysis shows similar specific surface for both synthesis routes. Methanol aerogels are very transparent and their shrinkage is smaller than that of acetone aerogels. The aerogels synthesised using acetone have a decreasing transparency as the precursor amount is lowered. Acetone-0·1 and acetone-0·2 show a clear white shading, meaning that there is some scattering of visible light, so there are a percentage of macropores with sizes similar to the visible frequency range. This is confirmed with a broader distribution of the pore size seen by SEM.

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