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Mass fractal characteristics of sonogels prepared from sonohydrolysis of tetraethoxysilane with additions of dimethylformamide

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Abstract

Wet silica gels with $\sim 1.4 \times 10^{-3}$ mol SiO_2/cm^3 and ~90 vol.% liquid phase were prepared from the sonohydrolysis of tetraethoxysilane (TEOS) with different additions of dimethylformamide (DMF). Aerogels were obtained by CO_2 supercritical extraction. The samples were studied mainly by small-angle X-ray scattering (SAXS) and nitrogen adsorption. Wet gels exhibit a mass fractal structure with fractal dimension D increasing from 2.23 to 2.35 and characteristic length ξ decreasing from ~9.4 nm to ~5.1 nm, as the DMF/TEOS molar ratio is increased from 0 to 4. The supercritical process apparently eliminates some porosity, shortening the fractality domain in the mesopore region and developing an apparent surface/mass fractal (with correlated mass fractal dimension $D_m \sim 2.6$ and surface fractal dimension $D_s \sim 2.3$) in the micropore region. The fundamental role of the DMF addition on the structure of the aerogels is to diminish the porosity and the pore mean size, without, however, modify substantially the specific surface area and the average size of the silica particle of the solid network.

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1. Introduction

A large variety of glass and glass ceramics has been obtained by sol–gel process from the hydrolysis of tetraethoxysilane (TEOS) [1]. The overall process evolves hydrolysis and polycondensation reactions leading to the growth of clusters that eventually collide together to form a gel. A mutual solvent such as ethanol is usually employed in the conventional sol–gel method as a homogenizing medium for the TEOS–water mixture. Sonochemistry is an alternative method to promote hydrolysis without using alcoholic solvents by submitting the acidified TEOS–water mixture to the action of ultrasound [2–4].

The structure and properties of the gels have attracted the attention of several researches for a wide variety of applications. Silica gels have been considered as appropriated matrices for the preparation of complex-center doped materials for a variety of metallic ions [5,6] and for encapsulation of a variety of organic [7–9] and inorganic compounds [10,11], with interesting optical and/or electronic properties. The mesoporous structure has been considered as an important transport medium for a variety of applications such as controlled-release carrier implantable materials for low weight drugs in biological systems [12,13] and as substitute materials for membrane processes in fuel cells [14].

Wet gels frequently exhibit a mass fractal structure consisting of a continuous solid network embedded in a great volume fraction liquid phase. The structural properties of the final product depend on the conditions of the hydrolysis, the aging and the drying of the gels. Supercritical drying (aerogels), freeze drying (cryogels), and evaporation drying (xerogels) are the usual methods in dried gel production. To favor the obtaining of monolithic pieces of dried

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gels, some drying control chemical additives (DCCAs) have been recognized, which can really act as structure modifiers [1]. *N*,*N*-dimethylformamide (DMF) has been considered as a basic DCCA structure modifier [15–17] because its relative low surface tension and its ability to form strong hydrogen bonds with the silanol groups of the silica gel. Although several studies deal with the influence of the additions of DMF on the structure of xerogels, only a few works deal with the influence of DMF on the structure of aged wet gels and on the structure of the resulting aerogel [16]. Besides that, typical preparation of the gels with different DMF/Alcoxide proportion frequently yields gel samples with different silica concentrations, which makes it dubious to attribute possible structural modifications exclusively to the influence of the DMF.

In this work, we prepared gels from the sonohydrolysis of TEOS with different additions of DMF, but the water/TEOS molar ratio and the reactant mixture volume were kept constant for all the DMF additions during the hydrolysis step of the process, and a determined water quantity was added after the hydrolysis step, in each case, in order to obtain silica sols with the same volume concentration of silica. The influence of the DMF additions on the structure of the gels was studied by small-angle X-ray scattering (SAXS) and nitrogen adsorption isotherms. An interesting correlation between the mass fractal characteristics of the aerogels as determined by SAXS and as deduced from the pore size distribution is presented.

2. Experimental

The samples were prepared from the sonohydrolysis of mixtures of tetraethoxysilane (TEOS), distilled and dionized water, and 0.1 N HCl as a catalyst, with additions of dimethylformamide (DMF) so that the DMF/TEOS molar ratio (R) was ranged according to $R = 0$, 2, 3 and 4. The proportion of the components in the mixtures was chosen according to Table 1 in order to obtain mixtures with the same water/TEOS molar ratio (~6.45) and approximately the same total volume (~38 ml) during the hydrolysis step of the process.

The hydrolysis was promoted during 10 min under a constant power (~0.7 W/cm^3) of ultrasonic radiation. The sol was diluted in adequate volumes of water (Table 1) in order to obtain final solution with the same silica concentration. The sonication was then continued for 2 min for complete homogenization. 3.5 ml of 0.1 N $NH_4(OH)$ was added to the pure TEOS sol ($R = 0$) in order to accelerate the gelation process by increasing the pH. The same base quantity was then added to each one of the silica sols in order to approach the conditions for gelation and aging of all the samples. The volume concentration of silica in the sols were estimated as 1.41×10^{-3} equivalents of Si per cm^3.

Table 1
Preparation of the silica sols with additions of DMF (non-specified errors are in ±0.1 cm^3)

R	Hydrolysis step				Sol dilution
	TEOS (cm^3)	H_2O (cm^3)	0.1 N HCl (cm^3)	DMF (cm^3)	H_2O (cm^3)
0	25.0	8.0	5.00 ± 0.05	0	37.9
2	17.2	3.9	5.00 ± 0.05	11.9	13.1
3	14.9	2.7	5.00 ± 0.05	15.4	5.8
4	13.1	1.8	5.00 ± 0.05	18.1	0

The resulting sols were cast in sealed containers and kept under saturated conditions for 30 days at 40 °C for gelation and aging. Monolithic pieces of wet gels were then obtained. The wet gels were characterized by density measurements, thermal gravimetric (TG) analysis, and small-angle X-ray scattering (SAXS).

For the obtaining of aerogels, the liquid phase of the wet gels was exchanged by ethanol at room temperature. The volume of the ethanol surrounding the gel, about 10 times the apparent gel volume, was exchanged each 24 h during 10 days. The ethanol was then exchanged by liquid CO_2 in an autoclave followed by supercritical CO_2 extraction. Monolithic 1 cm diameter 2 cm height cylindrical shaped samples of aerogels were obtained after the supercritical CO_2 extraction. The aerogels were studied by density measurements, nitrogen adsorption, and small-angle X-ray scattering.

The SAXS experiments were carried out using synchrotron radiation with a wavelength $\lambda = 0.1608$ nm. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining a pin-hole geometry. A 1D position sensitive X-ray detector was used to record the SAXS intensity as function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The experimental set allowed to get SAXS data from $q_0 = 0.13\ \text{nm}^{-1}$ to $q_m = 3.4\ \text{nm}^{-1}$ with a resolution of $\Delta q = 4.87 \times 10^{-3}\ \text{nm}^{-1}$. The data were corrected by the sample attenuation and the parasitic scattering, and normalized with respect to the beam intensity and the logarithm of the attenuation, which is proportional to the thickness of the sample.

The nitrogen adsorption isotherms were obtained at liquid nitrogen temperature, after degassing the aerogels at 200 °C for 24 h. The data were analyzed for the BET specific surface S_{BET}, the total pore volume per mass unit V_p, as the total adsorbed volume of nitrogen at a single point close the saturation pressure, the pore mean size $l_{BET} = 4V_p/S_{BET}$, and the pore size distribution (PSD), as determined by the classical Kelvin equation and the Harkins and Jura model for cylindrical pores [18].

3. Results

3.1. Wet gels

Table 2 shows the values measured for the density of the wet gels ρ_{wg} for $R = 0$, 2, 3, and 4. Fig. 1(bottom) shows the mass loss of the wet gels as determined by thermal