Colloidal aggregation phenomena:
Spatial structuring of TEOS-derived silica aerogels

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Abstract

In this contribution, the homogeneity of silica aerogels made from tetraethyl orthosilicate (TEOS) was studied by means of Fourier transform infrared (FTIR) and ^{29}Si nuclear magnetic resonance (NMR) spectroscopies. FTIR spectra show a slight difference in the asymmetric Si–O–Si stretching vibration frequency in the outer and inner part of the aerogels. According to the ^{29}Si NMR data, a higher relation Q^4/Q^3 was obtained in the inner parts of the gels compared with their outer parts, proving the difference in the cross linkage of the silica network. The obtained results are interpreted in terms of the specific spatial structuring of the colloidal suspensions due to the presence of gravity.
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Keywords: Silica gel; TEOS; Hydrogels; Aerogels; Microgravity

1. Introduction

Recently, many works have been devoted to the development of silica gels with controlled structural properties, which have found numerous ways into the synthesis of advanced materials. For instance, silica gels have relevant applications as diffusion–reaction systems [1–5]. The particular structure of the gels minimizes the effects of convection and precipitation, providing a diffusive mass transport medium similar to that formed in microgravity conditions [6–8]. Polysiloxane hydrogels have been used for many years as crystal growth media, which appear to be more effective than conventional agarose [9]. The diffusive transport properties of silica gels depend on the type and characteristics of the polymer network. Controlling the structural properties of this network, in particular, helps to plan crystal growth and improve the properties of the resulting crystals.

A sol, which forms a gel, is a colloidal suspension of solid particles in a liquid. According to the classical concepts of colloid chemistry, a colloid is a suspension in which the dispersed phase is so small (1–1000 nm) that the gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges. It has been shown that numerical models for colloidal aggregation consider both Brownian motion and the gravitational forces for the colloidal particles and clusters [10–12]. Allain et al. [10] have shown also that in colloidal suspensions, initially dispersed particles and clusters undergo Brownian motion. But further along in the process, the clusters may be large enough to settle under gravity, and then sedimentation alters the growth mechanism. So far, the investigation of the influence of gravity on the process of gelling could allow to optimize technologies and to obtain sol–gel derived nanomaterials with controlled structural properties.

In our previous work [13], we have experimentally shown the specific spatial structuring of TEOS silica aerogels. Briefly, the combination of small-angle X-ray scattering (SAXS) experiments with direct visualization techniques such as atomic force microscopy (AFM) and scanning electron microscopy (SEM), has indicated that the morphology, particle size, and fractal dimension of the TEOS aerogels depend on their position between the surface and the internal part of the corresponding wet gels. In this paper we offer further evidence of the spatial struc-

turing using the chemical information provided by ^{29}Si NMR and FTIR spectroscopies.

2. Materials and methods

The TEOS-derived silica aerogels described here were obtained using conditions listed in Table 1. The synthesis conditions were identical to those used in our previous work [13]. The silica alcosols were transferred into 13-mm-length and 45-mm-diameter test tubes and were tightly covered. After aging for 3 days at room temperature, the top and the bottom parts (10 mm thickness) of the alcogels were cut and supercritically dried. The infrared spectra were obtained in diffuse reflectance mode on a Bruker Tensor 27 Fourier transform infrared spectrophotometer (FTIR) in the 400–4000 cm^{-1} spectral range on KBr phase. The sensitivity of the measurements was set at 4 cm^{-1}. NMR measurements were performed on a Varian Unity 500 spectrometer and referenced to external tetramethylsilane.

3. Results and discussion

The FTIR spectra of the samples exhibited characteristic peaks of TEOS silica gels (Fig. 1). A broad band at 3400 cm^{-1} corresponded to molecular water hydrogen-bonded to each other and to SiOH groups. The 1630 cm^{-1} peak was due to the vibration of molecular water. The bands observed around 1090, 800, and 465 cm^{-1} were related to asymmetric, symmetric, and bonding modes of Si–O–Si bridging sequences, respec-

Table 1
Conditions of synthesis of the TEOS hydrogels

Sample	TEOS/EtOH/ H$_2$O (vol%)	EtOH/TEOS molar ratio	H$_2$O/TEOS molar ratio
TEOS1	15/0/85	0	65.6
TEOS4	15/18/67	5.4	51.7
TEOS2	15/36/49	10.8	37.8
TEOS3	20/39/21	13.3	12.1

tively [14]. The stretching vibration of free silanol groups on the surface of the aerogels took place at ∼960 cm^{-1} and the band at ∼560 cm^{-1} which is usually associated with siloxane backbone vibrations [15]. It has been demonstrated that a high frequency of the asymmetric Si–O–Si stretching vibration indicates a strongly cross-linked framework [16]. Table 2 shows changes in the frequency of the Si–O–Si band as a function of their spatial position. It can be seen that there is a slight difference in the peak frequency in the outer and inner part of the gels. Because the obtained shifts are situated in the range between 1 and 4 cm^{-1}, the sensitivity of our FTIR measurements do not allow us to determine the significance of this difference.

^{29}Si NMR was used in order to obtain quantitative structure information about the local surroundings of silicon atoms in the silica aerogels. We focused our measurements on the four possible resonance peaks for silica gels. These peaks are well known as Q^n ($n = 1, 2, 3, 4$), where n indicates the number of Si–O–Si linkages attached to silicon. Fig. 2 shows the ^{29}Si NMR spectra of the TEOS-derived aerogels. Peaks are observed with chemical shifts around −91, −101, and −110 ppm, denoting the presence of Q^2, Q^3, and Q^4 species, respectively [17]. Each spectrum was deconvoluted into three component peaks using Gauss–Lorentz curve fitting software (Varian NMR processing software), on which chemical shift and fraction are given in Table 2. As a measure of cross linkage, the ratio of Q^4 to Q^3 sites is compared, with higher ratios indicating stronger cross linking. Comparing the resonance spectra of the silica aerogels (Fig. 2 and Table 2), we can note that the distribution of silicon oxide species in outer and inner parts is different for all the samples. The relative intensity of the peak of condensed species Q^4, as well as the relation Q^4/Q^3, is higher in the TEOS4 system. Due to optimum ethanol content, the hydrolysis and condensation processes occur systematically, which gives rise to a cross-linked three-dimensional siloxane network. Therefore, it would be possible to suppose that the clusters will reach a large size quickly and eventually begin to drift down. In
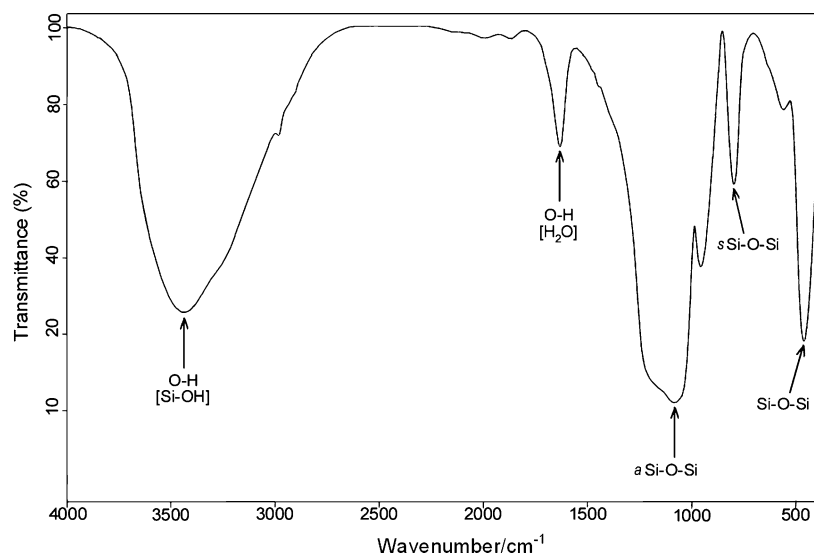

Fig. 1. Representative FTIR spectrum obtained from TEOS aerogels: outer part of the TEOS1 sample.

Table 2
Chemical shifts and fractions of Q^4, Q^3, and Q^2 species[a] and Si–O–Si peak position[b]

Sample	Q^4		Q^3		Q^2		Q^4/Q^3	Si–O–Si peak position (cm^{-1})
	(ppm)	(%)	(ppm)	(%)	(ppm)	(%)		
TEOS1								
Outer part	113.9	42.1	104.5	58.0	–	–	0.7	1087
Inner part	113.6	45.6	104.5	53.5	94.3	1.0	0.9	1089
TEOS4								
Outer part	112.9	66.5	103.6	33.5	–	–	2.0	1990
Inner part	113.0	79.2	103.7	20.8	–	–	3.8	1991
TEOS2								
Outer part	113.1	56.4	104.2	41.7	93.0	2.0	1.4	1089
Inner part	112.6	61.9	104.3	38.1	–	–	1.6	1093
TEOS3								
Outer part	114.0	49.2	104.5	48.2	93.8	2.7	1.0	1088
Inner part	112.9	56.1	104.6	42.1	93.6	1.8	1.3	1085

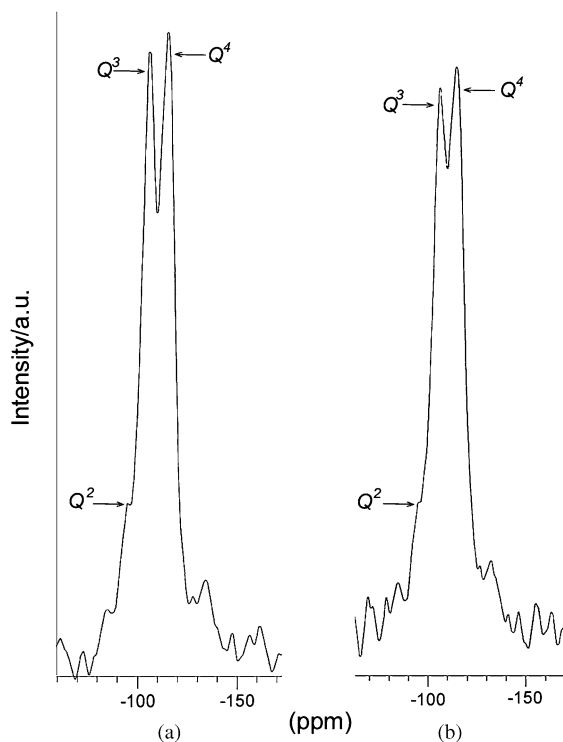[a] From ^{29}Si NMR measurements.
[b] From FTIR spectroscopy.

Fig. 2. Representative ^{29}Si NMR spectra obtained from TEOS aerogels: (a) outer part of the TEOS3 sample; (b) inner part of the TEOS3 sample.

consequence, the content of condensed species in the inner part of TEOS4 aerogel becomes significant.

The high-water TEOS1 system prepared without ethanol reveals a lower proportion of Q^4 species and Q^4/Q^3 relation. At high H_2O/TEOS molar ratio the rate of hydrolysis increases and at the same time the rate of polymerization decreases, which leads to cyclization and an increase in siloxane bond formation within the SiO_2 particles. The smaller size of formed particles diminishes their gravitational drift resulting in a narrower particle distribution between the surface and the internal part of

the sol. Hence, the increase of hydrolysis rate will enhance the gelation process, leading to the formation of a gel network by the packing of these particles. This explains a more uniform distribution of condensed species for the TEOS1 system.

In the TEOS2 and TEOS3 aerogels obtained at high EtOH/TEOS values, the relation Q^4/Q^3 decreases with on increase of the amount of ethanol. The excess of alcohol (molar ratio EtOH/TEOS > 6) separates intermediate products of polymerization and promotes separation of aggregates. The separation of aggregates reduces the degree of cross linking and leads to more open networks. As an increase in the content of EtOH reverses both the hydrolysis and condensation reactions, at equilibrium both the partly hydrolyzed and unhydrolyzed TEOS and the smaller size units of polymerized form, may exist. So that there was found a correlation between the high content of incomplete condensed Q^2 species for the TEOS3 aerogel and the excess of ethanol in the sol. The system TEOS3 with the higher ethanol content produces a gel when kept over 1 week; however, there is not a clear difference between the distribution of silicon oxide species in the outer and the inner parts. This finding can be explained as follows. Since the cluster nuclei are kept apart, their rate of growth is very sluggish, producing pore of increasing size. Gonzalez [18] attributes an increase in the fractal dimension of the big drifting clusters on the bottom to the trapping of the small clusters and single particles by this part. In our case, the less condensed small particles, which are abundant due to the gelation conditions, could statistically fill the space inside of the aggregate pores and between the aggregates. These trapped settling level of units off the subsequent depletion of the condensed species in the bulk of the sample TEOS3.

In conclusion, the reported results, in combination with the previous study on silica gel structural properties such as morphology, particle size, and fractal dimension, provide evidence of spatial heterogeneity of TEOS silica aerogels. In particular, FTIR and ^{29}Si NMR data showed a difference in the compactness of the silica network in the outer and inner parts of the prepared gels. We suggest that these phenomena can be due to the specific spatial structuring of the colloidal suspensions described in a series of numerical simulation works.

Acknowledgments

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