

Novel Ringing Silica Gels That Do Not Shrink

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Silica gels usually show the phenomena of syneresis. The gels shrink with time after preparation. This process is also observed with the gels that are prepared with the new Si precursor silicic acid tetrakis(2-hydroxyethyl) ester. It is shown that the shrinkage of the gels can be prevented if the cationic precursor *N*-[(trimethoxysilyl)propyl]-*N,N,N*-trimethylammonium chloride is added. The gelation process and the final structure of the gels were observed by rheological and SANS measurements. The gelation time is increasing with the concentration of the cationic precursor. After mechanical stimulation the gels are ringing in audible frequencies. This effect is explained by the high value of the storage modulus G' of the gels and the ratio of G' over G'' (loss modulus). Increasing cationic precursor concentrations lower the audible frequencies. The wet silica gels were supercritically dried by CO_2 and characterized by FE-SEM and BET-measurements. From the surface area the radius of the SiO_2 -particles was calculated and was in the range between 9.5 and 12.3 nm.

Wet and dry silica gels are the subject of intensive investigations because of their fascinating properties for a variety of technical applications.^{1–3} In both states the gels can have large internal surfaces in the area of $1000 \text{ m}^2/\text{g}$.⁴ They can be prepared as large monoliths. In the dry state they can have a density as low as 0.02 g/cm^3 . Usually the gels are prepared from TEOS or TMOS emulsions in water. Both compounds can be emulsified and subsequently hydrolyzed in aqueous solution to silicic acid, which then, in a slower reaction, condenses into the silica gels. They also can be prepared from water soluble Na-silicates and an acid that is strong enough to neutralize the silicate to silicic acid. In both cases fine silica particles are formed (sols), which then condense into a three-dimensional network. The wet gels are usually completely transparent, optically isotropic materials that get and maintain the shape of the preparation vessel. With time, however, the network ages and shrinks. During this process the network contracts and separates from the wall. The process is called syneresis.^{5–7} As in other gels it is due to strong attractive forces between the gel beads. In other gels the swelling and shrinkage of gels can be a rather fast process and the gels can rapidly accept an equilibrium situation in which repulsive and attractive forces balance each other. In silica gels, the network is rather stiff and the elasticity moduli are high in the range of 10^5 Pa . For this reason the gels can only slowly change their shapes. To prevent the gels from shrinkage, repulsive forces have to be placed on the gel structures. This can indeed be accomplished by attaching ionic charges on the silica network. In the following we describe how this can be done. We also describe the properties of the resulting silica gels.

Recently we have described a simple method of preparing silica gels⁸ from the precursor silicic acid tetrakis(2-hydroxyethyl) ester that had been synthesized from TEOS and glycol.⁹ This precursor is a water soluble compound, and when dissolved in water, it hydrolyzes into glycol and silicic acid, which then condenses into silica gels. In comparison to other gel-forming processes, this method has two advantages: The whole process occurs in a single homogeneous phase and glycol is produced during the hydrolysis instead of methanol or ethanol. The last two solvents lead to a reduction of the solvophobic effect, which

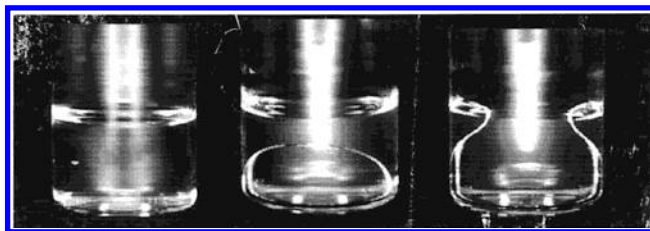


Figure 1. Process of shrinkage: Left sample shows no shrinkage. The sample in the middle started retreating from the wall of the glass vessel several days after preparation. After some weeks the gel (on the right) is nearly completely separated from the wall. Samples contain 50 wt % Si precursor.

means the self-organization of hydrophobic molecules such as the micellization of surfactants into micelles is hindered while glycol hardly affects this.

The gels that have been produced by this method otherwise have similar properties as silica gels, which are produced by other methods; in particular, they shrink with time in the wet state (Figure 1).^{10–12} To prepare silica gels with ionic charges on the network, we added small amounts of a cationic precursor *N*-[(trimethoxysilyl)propyl]-*N,N,N*-trimethylammonium chloride to the neutral precursor. We observed that the gelation proceeded in the same way as without the new precursor but the gelation time increased. There was one major difference: The thus prepared silica gels no longer shrunk when the ionic precursor was between 0.3 and 5% of the main precursor.

In Figure 1 the process of shrinkage is shown. The sample was produced without the cationic precursor. About 7 h after mixing equal weights of Si precursor and H_2O , the sol–gel-transition could be observed. This gel is shown on the left of Figure 1. At this stage the gel is ringing in audible frequencies after mechanical stimulation. Thirty-two hours after preparation this phenomenon disappeared, which indicates that the network contracts and separates from the wall. The sample in the middle started retreating from the wall of the glass vessel. The picture of the gel on the right was made some weeks after preparing. The gel separated nearly completely from the wall. When small amounts of the cationic precursor were added to the neutral

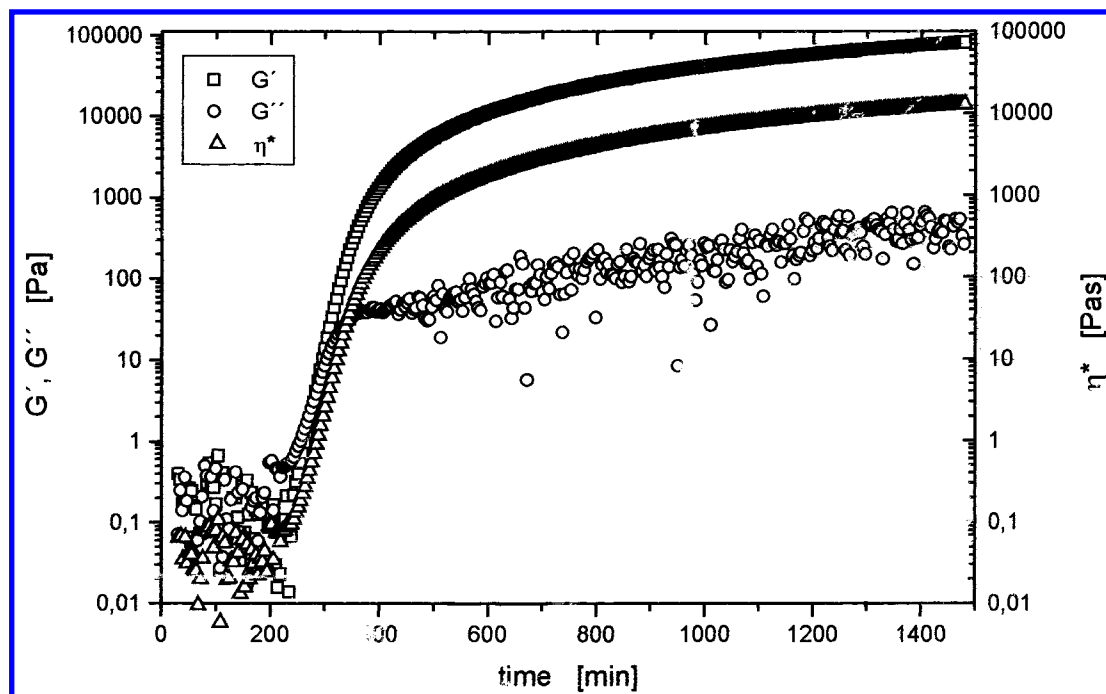


Figure 2. Oscillating rheological measurement (cone-plate geometry with a constant frequency of 1 Hz and a strain of 1%) following the gelation of a sample with 50 wt % Si precursor and 0.2 wt % cationic additive.

TABLE 1: Space of Time of G'/G'' Crossover after Preparation and Value of G'/G'' Crossover with Dependence on the Amount of Cationic Precursor

cationic precursor concn (wt %)	G'/G'' crossover (min)	G'/G'' crossover (Pa)
0	160	0.10
0.1	201	1.50
0.2	279	3.05
0.3	347	3.87
0.4	455	8.00
0.5	492	12.49
0.6	809	14.60
0.7	1006	15.40
0.8	1376	23.87
0.9	1760	20.60
1.0	2024	20.87

^a Samples contain 50 wt % Si precursor.

precursor, the shrinkage of the gel can be prevented and the shape of the gel remains, as shown on the left of Figure 1.

The cationic precursor has an impact on the gelation time of the systems. In Figure 2 we show results of rheological measurements where the gelation of the samples was followed with oscillating rheological measurements from which the complex viscosity and the storage and loss moduli can be determined. The gelation time can clearly be derived from these measurements as the time where the storage modulus increases abruptly and crosses over the loss modulus.

The data (Table 1) show that the gelation time is increasing strongly with the concentration of cationic precursor in the sample. Actually, we have observed that the gelation is completely suppressed when the concentration of the cationic precursor is higher than 5 wt %. Obviously in this situation the gelation time goes to infinity when the concentration of the cationic precursor reaches a critical concentration C^* .

The data in Figure 2 show that the systems remain in a low viscous state for a long time. In this state the storage modulus is so low that it cannot be measured. Obviously the network has not yet developed. It is, however, likely that the precursor has been completely hydrolyzed and SiO_2 clusters from the

silicic acid have developed. The gelation time can be considered to be the time where the different clusters connect to one supra-molecular cluster spanning the whole sample. The hydrolysis of the precursor can be measured by ^1H NMR measurements.^{13–15} The rate constant depends on the pH. Under neutral condition the precursor has been completely hydrolyzed within a few minutes. The hydrolysis and condensation reaction occur in different time ranges.

With this gelation mechanism in mind, it is easy to understand the influence of the charged *N*-[(trimethoxysilyl)propyl]-*N,N,N*-trimethylammonium chloride precursor on the whole process. We can assume that the hydrolysis reaction and the condensation of the hydrolyzed precursor proceeds with about the same rate as for the precursor without the cationic group. The cationic group, however, cannot react with another group and for this reason accumulates on the surface of the cluster. In this way the cluster can, for a high enough ratio of modified to unmodified precursor, reach a situation in which the whole surface of the cluster is saturated with cationic groups and a gel can no longer be formed. For small ratios the cluster can still react with each other and form a supramolecular structure.

The process of gelation and the final structure of the gel can be monitored by small angle neutron scattering (SANS).¹⁷ Figure 3 shows an example of a time-dependent measurement of the plot of scattered intensity I , versus scattering vector q of a sample containing 50 wt % Si precursor. The increase of the intensity at low q with time indicates the formation of a fractal structure, as observed by other gelation processes.¹⁸ It was shown before that the fractal dimension of a particle can be determined from the slope of the log–log plot.^{8,16} $I(q)$ is of a power-law form $I(q) \sim q^{-D}$. The exponent D is related to the fractal dimension of the scattering structures. Depending on the value of D , it is possible to distinguish between diffusion-limited aggregation (DLA; $D \approx 1.8$) and reaction-limited aggregation (RLA; $D \approx 2.1$).¹⁹ After correction for the solvent the slope of the double log plot leads to a measured fractal dimension of 2.2, which is, within error, comparable with $D \approx 2.1$ calculated for the RLA model.

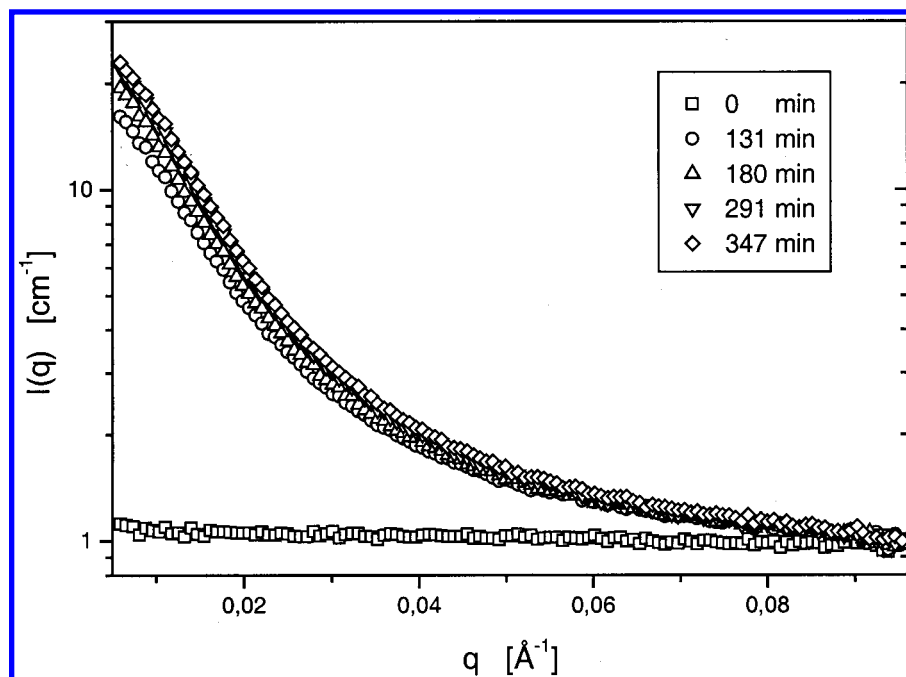


Figure 3. Time dependent small angle neutron scattering measurements of the gelation for a sample containing 50 wt % Si precursor without cationic additive.

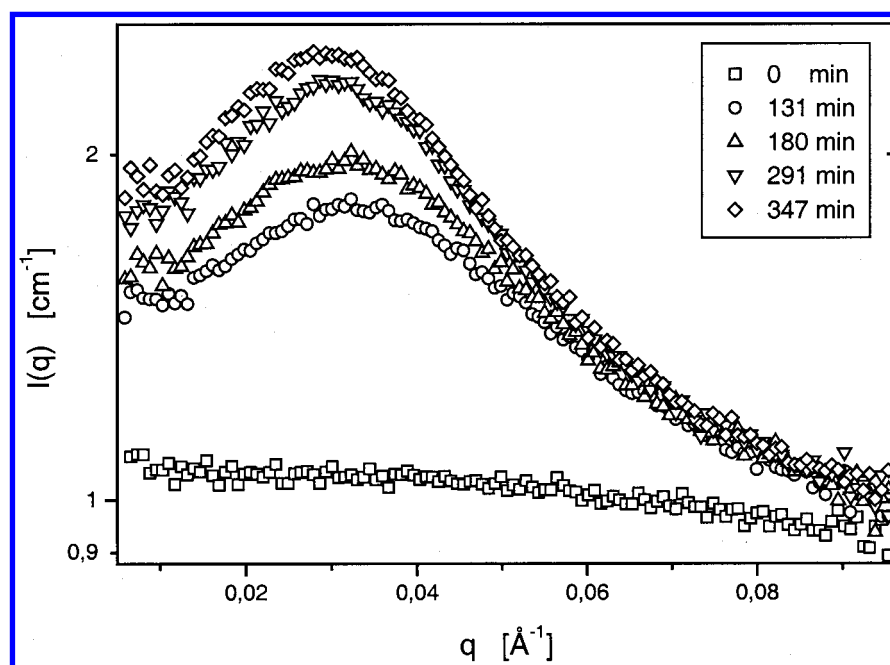


Figure 4. Time dependent small angle neutron scattering measurements of the gelation for a sample containing 50 wt % Si precursor and 0.4 wt % cationic additive.

The scattering pattern of a sample that was produced with a charged Si precursor added to the system is completely different and shows a correlation peak (Figure 4). It is likely that the scattering peak is a consequence of the repulsive interaction between the cluster. They try to get away from each other as in the similar situation of ionically charged micelles or latex particles and the system sets up a nearest neighbor order with a spacing of $d = 2\pi/q_{\text{max}}$, when q_{max} is the scattering vector at maximum intensity. The maximum of the correlation peak is at about 0.3 \AA^{-1} , which leads to a distance of 21 nm between the scattering clusters. This value corresponds to the results of the SEM investigations (see later). Since in the final gel state the individual clusters are connected to each other, the situation is more comparable to the situation in viscoelastic surfactant

solutions with charged threadlike micelles and d is the mean spacing between the entangled rods.

The gels give off a metallic sound when they are tapped with a finger or a soft object. This phenomena was also noticed by other groups.^{20–22} The ringing phenomena disappears when the gel starts shrinking. Similar properties have been observed with surfactant mesophases at high concentrations. These systems have been called ringing gels.^{23,24} The effect is due to the fact that the storage modulus of the system is high enough to give vibrations in the audible frequency range and the loss modulus is several decades lower than the storage modulus, so it takes many oscillations of the order of G'/G'' before the elastic energy stored in one vibration is transformed into heat. The surfactant system that showed the phenomena were in the liquid crystalline

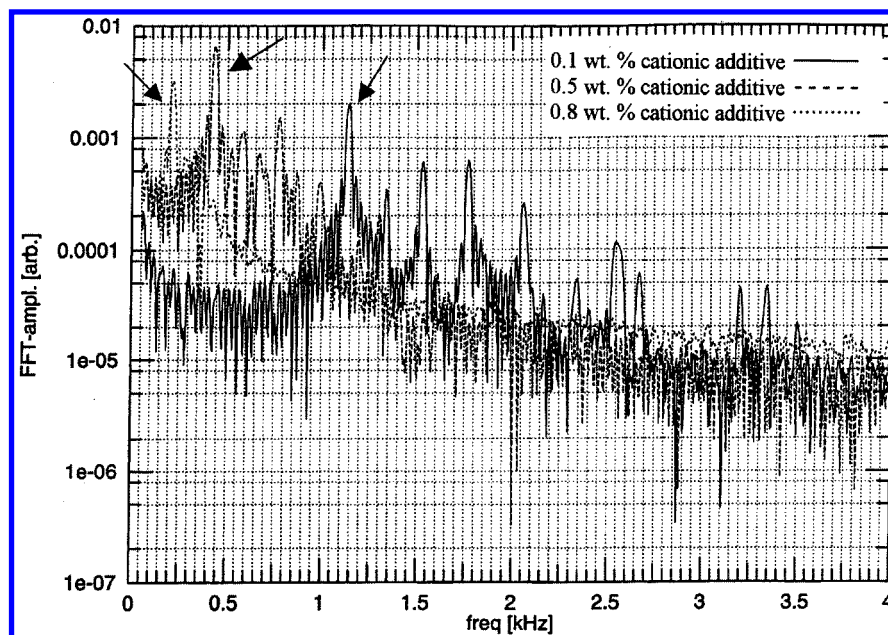


Figure 5. Sonogram of three different samples (containing 50 wt % Si precursor) with varying amounts of cationic additive. The lowest fundamental frequency is marked with an arrow.

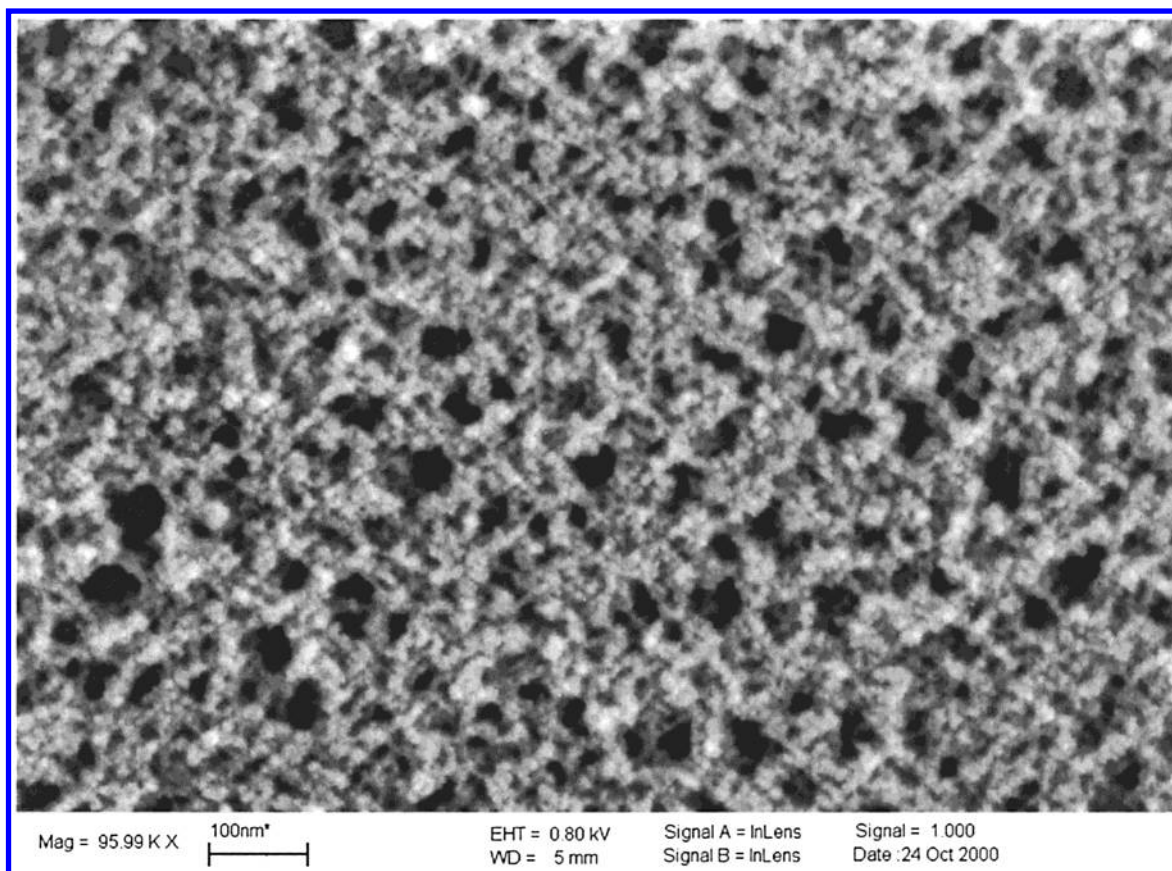


Figure 6. SEM of a supercritical dried silica gel containing 50 wt % Si precursor. The porous structure of the three-dimensional network can clearly be seen. The diameter of the pores varies from 5 to 30 nm.

state; actually, they were cubic phases. The ringing in the silica gels shows that the structure of the phase is not important for the phenomena. It is the values for G' and G'' that must have the right size for the phenomenon to occur. To make quantitative measurements on the phenomena, we recorded the sound waves with a microphone and a transient recorder and passed the recordings through a frequency analyzer. A typical sonogram is shown in Figure 5. It shows that the sound is a superposition of several frequencies. The lowest fundamental frequency that

also determines the height of the audible sound depends very much on the concentration of the cationic precursor when all other parameters of the samples remain constant. Increasing cationic precursor concentrations lower the audible frequency. The evaluated parameters are given in Table 2.

In Figures 6 and 7 FE-SEM pictures are shown. The pictures were taken from a small piece of silica that had been supercritically dried. At first the glycol and water of the wet gel had been replaced by acetone, and finally, the acetone had been

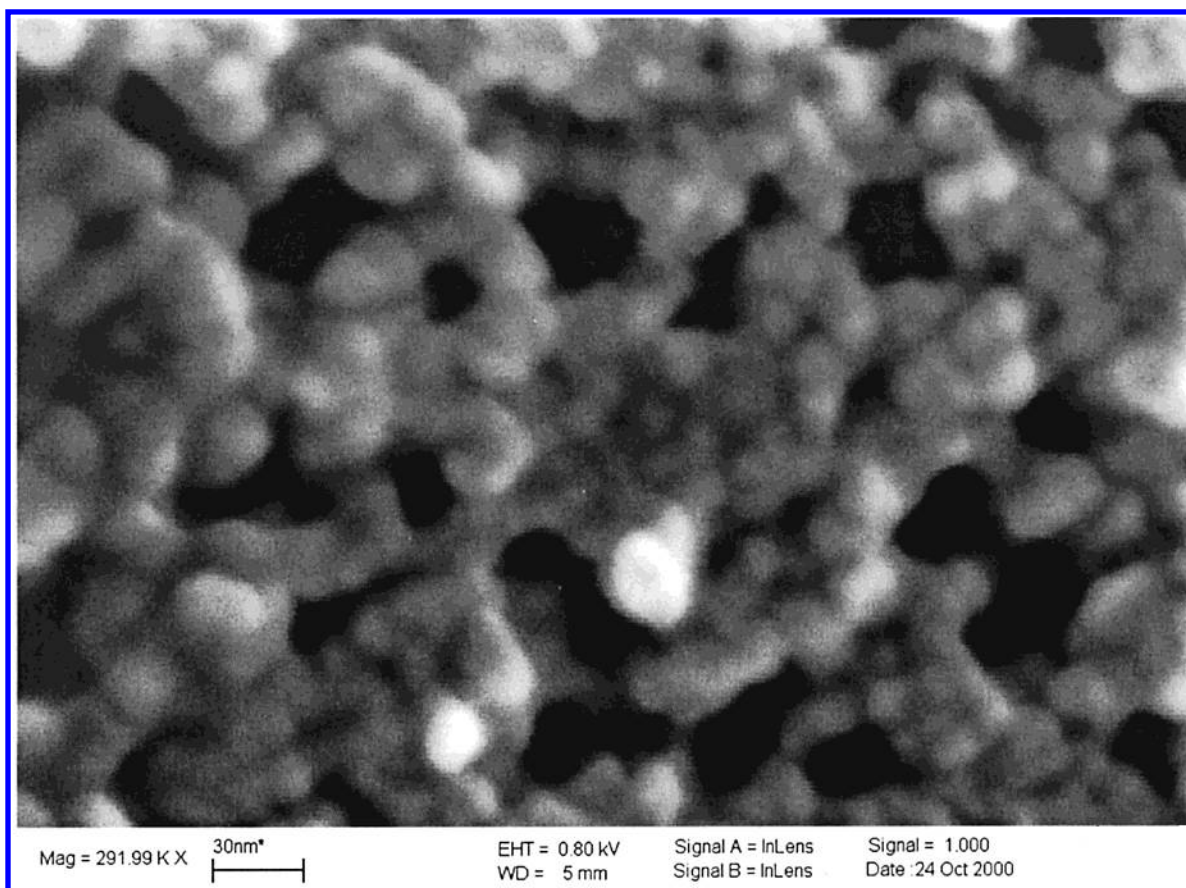


Figure 7. SEM of a supercritical dried silica gel containing 50 wt % Si precursor. The network consists of primary SiO₂ particles of about 5–20 nm diameter.

TABLE 2: Lowest Fundamental Frequency of the Ringing Gels after Mechanical Stimulation with Dependence on the Amount of Cationic Precursor

cationic precursor concn (wt %)	lowest fundamental frequency (Hz)
0.1	1140
0.5	440
0.8	210

^a Samples contain 50 wt % Si precursor.

exchanged for liquid CO₂.²⁵ The micrograph clearly shows that the gel consists of particles of about 10–20 nm diameter. These particles form a three-dimensional network. The micrograph looks very similar as SEM pictures from SiO₂ gels that have been published by other groups.^{26–30} Obviously, the structure of the gel does not depend very much on the method that was used for the preparation. The main features of the silica gels can easily be produced by a simple model, which allows us to calculate a radius of the primary particles from the surface area of the dried gel. The surface area A has been determined by BET measurements and is in the range of 1000 m²/g. We thus obtain the following equation

$$\frac{N4\pi R^3\eta}{3} = m$$

$$N4\pi R^2 = A$$

$$R = \frac{3m}{A\eta}$$

where N is the number of particles, R is the radius of the particles, η is the density, and m is the mass of silica in the

TABLE 3

cationic precursor concn (wt %)	mass after supercrit drying (g)	density (g/cm ³)	specific surface (m ² /g)	radius of Si cluster (nm)
0	1.111	0.272	996	12.3
0.2	0.540	0.157	955	10.8
0.5	0.570	0.187	871	10.5
1.0	0.553	0.213	795	9.8
1.5	0.556	0.227	776	9.5

sample. This very simple calculation leads to radii between 12.3 and 9.5 nm (Table 3). With increasing amount of cationic additive, the radius of SiO₂ cluster decreases. A reason for this could be that after a certain amount of cationic Si precursor is incorporated on the surface of the SiO₂ cluster the growth of the cluster is slowed or stopped. The calculated value for the radius is in good agreement with the value determined by SANS measurements.

In summary, the properties of silica gels which do not shrink because of the use of a cationic additive are reported. Normally, wet silica gels made from silicic acid tetrakis(2-hydroxyethyl) ester shrink within a short time after preparation. This process can be avoided by adding small amounts of cationic precursor (*N*-[(trimethoxysilyl)propyl]-*N,N,N*-trimethylammonium chloride), thereby increasing the number of ionic charges in the network and consequently the repulsive forces between the SiO₂ cluster. The use of the cationic Si precursor prolongs gelation time in comparison to the system without additive and leads to gels that are ringing in audible frequencies after mechanical stimulation. The frequency of the ringing and the structure investigated by SANS and SEM is strongly influenced by the amount of cationic Si precursor.

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