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Microstructure of silica gels by transmission electron microscopy

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Abstract. Transmission Electron Microscopy observations of dried silica gels are reported. The samples observed were prepared either by hydrolisis of alkoxides or by gellation of colloidal silica. Some experimental results concerning the porous structure of the samples are backed by the TEM results. The sample preparation procedure for TEM work is also discussed.

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1. Introduction

The scientific and technological interest in the "sol-gel route" for preparing ceramics and monolithic glasses has strongly increased in the last few years [1,2]. In particular, a rather extensive work has been dedicated to the study of the porous structure of some aerogels and its relation to the physical and chemical properties of those materials [3]. Despite of the existence of some other very powerful techniques, such as low angle X-ray and neutron scattering, the Transmission Electron Microscope (TEM) has proven quite useful for visualizing the structure of such materials to a very high detail in terms of spatial resolution [4,6]. Certainly, standard porosimetry measurements (Hg intrusion or N_2 absortion, for example) are still an invaluable tool for establishing the pore distribution of materials, but some direct observations of the actual spatial structure of the samples could give some help for the study of gels and related materials.

This present work is directed to the observation of the porous structure of some silica gels formed under various chemical and physical conditions. The technique used in our case was the TEM on powdered samples. We report the structural differences observed as a function of the preparation procedure and of the sintering processes as well. A brief discussion of some of the possible interpretation of the observations is also included.

2. Experimental

In this report, gels were formed by hydrolisis of alkoxides [6,7] and by gelling of a LUDOX-KASIL solution (LUDOX is a trade mark of Dupont's colloidal silica and KASIL is a 38% K_2O and 62% SiO_2 solution). The detailed procedure for preparing the gel samples under different chemical and physical conditions has been described elsewhere [6]. These techniques allows one to obtain either polymer-like or particle-like structures in the resulting gels. Also, various sintering temperatures were utilized to densify the original highly porous materials and then follow, in a partial form at least, the change of the porosity as a function of temperature and densification procedure.

On the other hand, TEM analysis of gel specimens presents a number of difficulties, mainly due to the scarcity of suitable sample preparation techniques for TEM work and to the strong interaction of the sample with the electron beam. A number of different techniques have been reported for preparing material for TEM observation. In particular, in the case of porous gels, some authors have described preparation methods for monolithic gels [7,8]. However, most of the reported techniques (like chemical etching, ion bombardment, cryomicrotomy, replicas, etc.) either introduce changes in the original microstructure of the samples or offer only a very partial picture of such microstructure. As for the interaction with the electron beam, there exist some reports describing typical structural changes introduced in a pure silica sample by electron irradiation, such as beam-induced crystallization in some cases and bubble formation under some other conditions [9,10]. These reports could serve as a qualitative guide during the interpretation of the TEM results.

In our case, in order to minimize as much as possible the structural changes during the preparation procedure, the gel specimens were powdered in a common laboratory mortar, then suspended in water and deposited onto carbon-covered microscope grids for TEM analysis. As a result, small gel particles were observed in the microscope with sizes ranging from few a μm to hundreds of μm in some cases. Many of the edges of the resulting particles were thin enough for TEM observation. A similar preparation technique has been successfully used in the observation of microcrystalline regions in common fused silica [10].

Because of the serious charging problem in the Electron Microscopy of the gel specimens, a very thin carbon layer was evaporated on top of some of the gel-containing microscope grids. The machine used for the TEM observations was a 300 KeV microscope (Phillips 430). At this stage, it must be pointed out the convenience of the use of medium accelerating voltages, *i.e.* between 200 and 400 KeV, for penetration and damage-reduction purposes [10]. A 100 μm diameter objective aperture was utilized to form the actual image in the electron microscope and the nominal spherical aberration coefficient of the machine is of about 1.2 mm. The use of this particular aperture allows one to guarantee the level of resolution necessary for our investigations

Finally, mercury porosimetry was used for pore diameter distribution and surface area measurements in all the samples prepared and the detailed results have been published in a separate report [6,15]. In this present work, the porosimetry

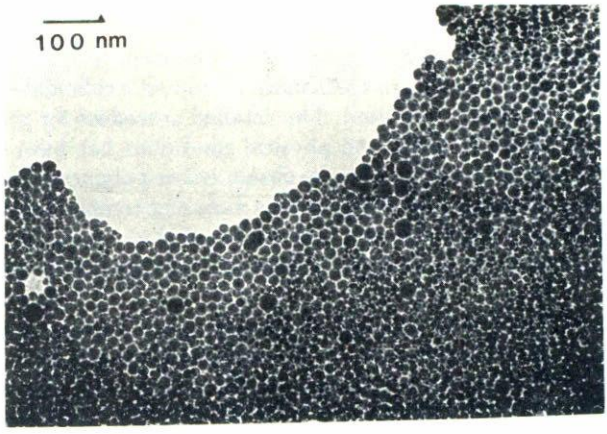

FIGURE 1. Medium magnification Transmission Electron Microscopy image of the coloidal silica particles (LUDOX) used in the present study.

was used as a reference for comparison with the TEM results and will be reported separately.

3. Results and discussion

In Fig. 1 we show a micrograph of the LUDOX particles used in this report for preparing the colloidal-like gels. The nominal diameter of the particles, according to the manufacturer, is of about 125 Åbut they were actually found to be larger than the quoted value by a factor of approximately 1.7. This disagreement coincides qualitatively with some previous reports on TEM studies of this type of particles where other authors found a larger particle radius as well [4]. Also, it is important to notice that, rather than a uniform particle size, there is a distribution of diameters. The latter can be better observed in the higher magnification micrograph of Fig. 2. This size distribution could be important for the subsequent preparation of gels, affecting the porosity and consequently the mechanical strength of the products [11].

The diagram of Fig. 3 schematically shows the measured pore sizes of one set of porous gels prepared by the hydrolisis of alkoxides at different heating rates and PH of the starting solution; for this set of samples the water to silica ratio was H_2O/SiO_2=10 [6,15]. The porosity was measured by BET as has been explained in a previous publication [6]. The diagram shows how the rapidly-heated samples presented smaller porosity in the case of base solutions. It also demonstrates the significant influence of the PH of gelation on the final product. Also, it is important to notice the increase in pore size with temperature. As for the case of the polymer-like gels, this effect could be explained by the Scherer's model for densification of gels prepared from metal alkoxides [13]. According to this model, based on a geometry

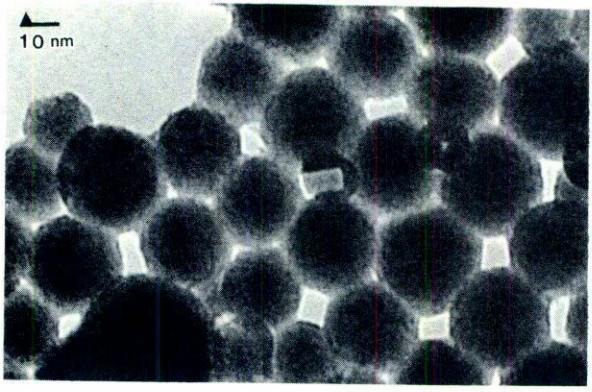

FIGURE 2. Higher magnification TEM micrograph of the same silica sample. Observe the size distribution of the particles.

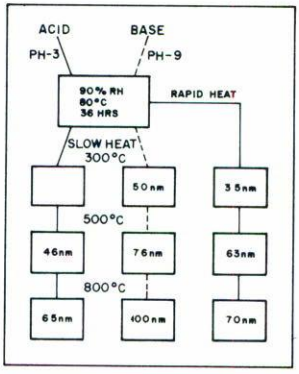

FIGURE 3. Schematic diagram of the preparation conditions and pore sizes of sol-gel glasses.

consisting of a cubic array of intersecting cylinders, the viscosity of the skeletal phase. The later would have the effect of reducing free volume [13]. Some results in the literature support, al least partially, this explanation [13–15].

The firing procedure also has a strong influence, not only in the final pore distribution but also in the formation of crevices and fissures [14]. This last point is illustrated in Figs. 4 and 5 that show two micrographs of alkoxide $H_2O/SiO_2=10$. Fig. 4 corresponds to a sample fired at 800°C for 6 hours and shows the presence of small crack in the bulk structure of the gel. Another interesting finding is that

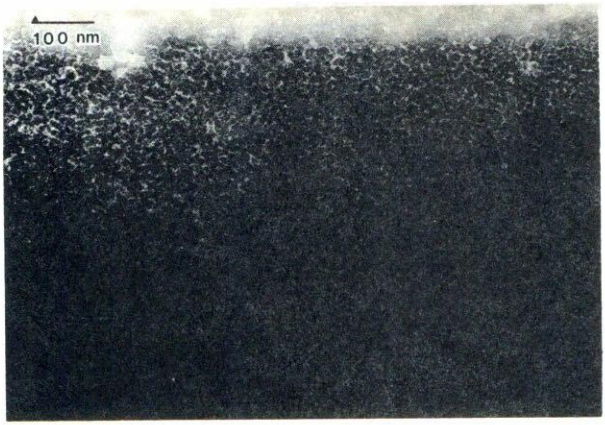

FIGURE 4. TEM micrograph of a sol-gel glass fired at 800°C for 6 hours. Notice the presence of micro-cracks in the structure.

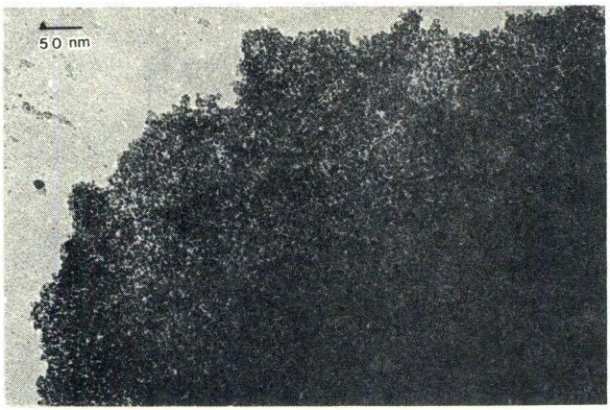

FIGURE 5. TEM micrograph of a sample pre-heated at 300°C (1 hour) and then fired at 875°C (6 hours). No cracks were observed in this case.

samples pre-heated for 1 hour at 300°C and then fired at 875°C for another 6 hours, did not show the cracking, as can be observed in Fig. 5.

Since the LUDOX particles are mainly composed of an anhydrous core, they would undergo very little skeletal densification. Thus, a model proposing the reduction of particle size as an explanation for the increase in pore size, is unlikely. What probably happens is a change in the morphology of the gel, going from a random array of spheres to an array of cylinders. This would produce the smallest pores to link together to form bigger pores. Fig. 6 shows the TEM micrograph of a

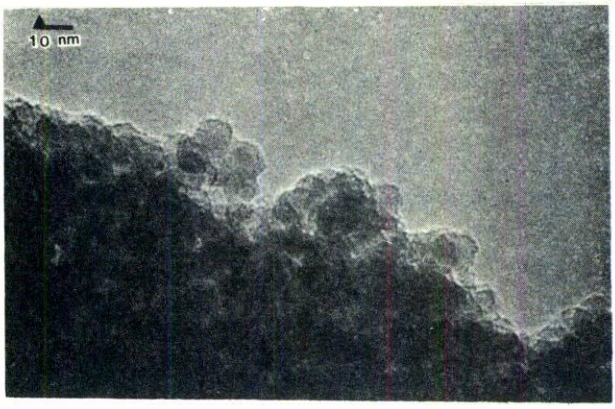

FIGURE 6. TEM micrograph of a LUDOX/KASIL = 90/10 sample sintered at 400°C.

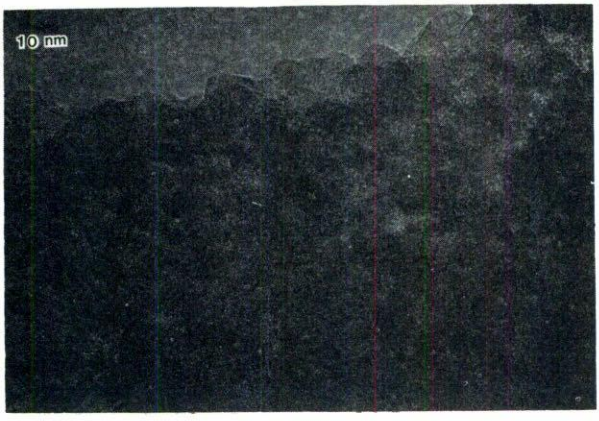

FIGURE 7. TEM image of a gel sample fired at 800°C. Notice that the necking is more visible as compared with the previous samples.

LUDOX/KASIL = 90/10 sample sintered at 400°C with a clear particle-like structure. As expected, there is an incipient necking of some of them. When the firing temperature is increased the necks are much more visible, as shown in fig. 7 (T=800°C) supporting the model proposed above.

The TEM observations are in good agreement with some other results reported in the literature and obtained by several other techniques. Thus the Transmission Electron Microscope is a powerful tool for analyzing the microstructure of monolithic and still-wet gel. Also, the use of more sophisticated TEM techniques (*i.e.* dark field,

side-band imaging, micro-diffraction, topographic contrast, etc.) are yet to be proven in the study of these materials.

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Resumen. Se reportan observaciones por microscopía eletrónica de transmisión de la microestructura de geles secos de silice preparados por hidrólisis o por gelación de silice coloidal. Los resultados apoyan experimentos previos sobre la estructura porosa de estos materiales. También se discute el procedimiento de preparación de muestras para microscopía electrónica.