

## Silica Morphology Characterized by SEM. The Effects of the Solvent Treatment and the Drying Process

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Foram investigados, através de microscopia eletrônica de varredura (MEV), os efeitos de tratamentos com os solventes água, propanona, etanol, metanol e éter etílico e de processos de secagem em forno de microondas, estufa, dessecador a pressão reduzida e liofilizador na morfologia de sílica gel. A sílica gel foi obtida de uma solução de silicato de sódio diluída a 1:5 (m/m SiO<sub>2</sub>:H<sub>2</sub>O). Os resultados indicaram que o processo de secagem em liofilizador conserva a estrutura do precipitado. O tratamento com solventes voláteis não altera a forma dos agregados, mas influi efetivamente na rugosidade.

Scanning electron microscopy (SEM) was used to investigate the effects of volatile solvents (such as water, propanone, ethanol, methanol or ethyl ether), treatment and drying processes, microwave ovens, drying ovens, and vacuum desiccators or freeze driers, on silica morphology. Silica gel was obtained from diluted sodium silicate (1:5 w/w SiO<sub>2</sub>:H<sub>2</sub>O). The results showed that the drying process based on freeze drying is more efficient for structural conservation of the precipitate. Treatment with volatile solvents does not change the shape of the aggregates, but has an important role in the determination of aggregate surface roughness.

**Keywords:** silica, morphology, drying, SEM

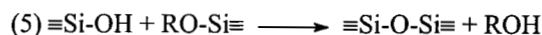
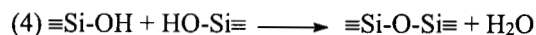
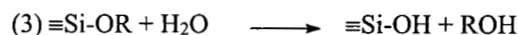
### Introduction

Silica is of interest in various fields including ceramics, glasses, catalysis, chromatography and colloids<sup>1,2</sup>. Particle morphology (shape and surface roughness) and size are important features for silica applications. These two parameters depend on the process of silica preparation. The sol-gel process is one of the most commonly used methods for obtaining silica. Usually the precursors are alkali metal soluble silicates<sup>2</sup> or silicon alkoxides<sup>3,4</sup>, both of which undergo hydrolysis and polycondensation reactions:

#### Silicate Solutions<sup>2</sup>



#### Alkoxides Solutions<sup>3</sup>



where R = alkyl group.

The drying process, as well as the nature of the solvent used for gel washing can be very important in particle solubility and in the surface properties, and particle and aggregate morphologies.

When silica gel is kept in the original liquid, its structure and properties continue to change long past the gelling point. This process is called aging<sup>5</sup> and it may include four stages, occurring separately or simultaneously: a) polycondensation (Eqs. 2, 4 and 5), b) syneresis (spontaneous shrinkage of the gel), c) coarsening or Ostwald ripening (an irreversible decrease in the surface area through dissolution

and reprecipitation processes), and d) phase transformation.

Of these stages, coarsening is one of the most important processes in particle and aggregate morphology. The rate of coarsening is a function of factors that affect solubility, such as temperature, pH, concentration and the type of solvent used in the after-treatment of the hydrogel<sup>6</sup>.

Changes during the drying process are due to the solid-liquid interfacial energy which can give rise to large capillary forces causing fractures on gel microstructures<sup>7</sup>.

According to the Gibbs-Kelvin equation<sup>5,6,7</sup>, for the gel aging and drying stages, the relative solid solubility and solvent vapor pressures are given by Eqs. 1 and 2, respectively:

$$S = S_0 \exp(2\gamma_{SL}V_m/RT_r) \quad (1)$$

$$P_s = P_0 \exp(2\gamma B/RT_r m) \quad (2)$$

where,  $S$  = fine particle solubility,  $S_0$  = solubility of the flat surface,  $V_m$  = molar volume of the solid,  $\gamma_{SL}$  = solid-liquid interfacial energy,  $R$  = ideal gas constant,  $T$  = temperature,  $r$  = surface radius of the curvature,  $P_s$  = vapor pressure over the solvent meniscus in the pore,  $P_0$  = liquid vapor pressure over a flat surface,  $B$  = molar volume of the liquid,  $\gamma$  = solvent surface tension, and  $r_m$  = radius of the curvature of the meniscus. Solid solubility is mainly a function of interfacial surface tension ( $\gamma_{SL}$ ) and size ( $r$ ), while solvent vapor pressure in the pores of the aggregate is enhanced due to the curvature.

Most silica preparation and drying up to now has been carried out by gel washing and aging with water. However, an alternative is to treat the silica gel with organic solvents<sup>2</sup>. This paper reports SEM results of silica gel treated with different solvents and dried by four different methods.

## Experimental

Commercial sodium silicate solution H 300 NDL (ICI Brasil, atual Inds. Gessy Lever Ltda - Div. Crosfield) with a  $\text{SiO}_2:\text{Na}_2\text{O}$  ratio equal to 5.56 was diluted with water to 1:5 (w/w  $\text{SiO}_2:\text{H}_2\text{O}$ ). Silica gel was obtained by the addition of HCl (P.A. Merck)  $3.0 \text{ mol dm}^{-3}$  to 50 g sodium silicate solution until a pH of ca. 0.5, under stirring at room temperature in a transparent polystyrene flask.

The gel that was obtained was then washed five times (5 min each) with deionized water by centrifuging at 2500 rpm (bench centrifuge Fanen 315). The precipitate was dialyzed against deionized water for one week, and the water was changed every 12 h. A chloride test was carried out in the dialysis water with  $\text{AgNO}_3$  ( $1.0 \text{ mol dm}^{-3}$  solution). Dialyzed gel was centrifuged and divided into two parts for solvent treatment and drying. The first part was divided into four samples which were dried in either a modified domestic microwave oven (White Westinghouse EM 900 1350 Hz) for 2 h, a laboratory drying oven (Fabbe

315) for 12 h, a vacuum desiccator under water vapor pressure with silica-gel as the desiccant for 5 weeks (840 h), or a freeze drier (MLW-LGA 05) at  $-20^\circ\text{C}$  and ca. 5 mmHg, for 12 h. The second part was divided into five samples each of which was suspended in either ethanol, methanol, propanone, ethyl ether (all solvents were P.A. grade Merck), or deionized water, and sonicated for 5 min (Ultra sound bath Thorton T-14 40KW, 60 Hz). All suspensions were left undisturbed for 24 h and then centrifuged, and then each was dried by the methods described for the first part.

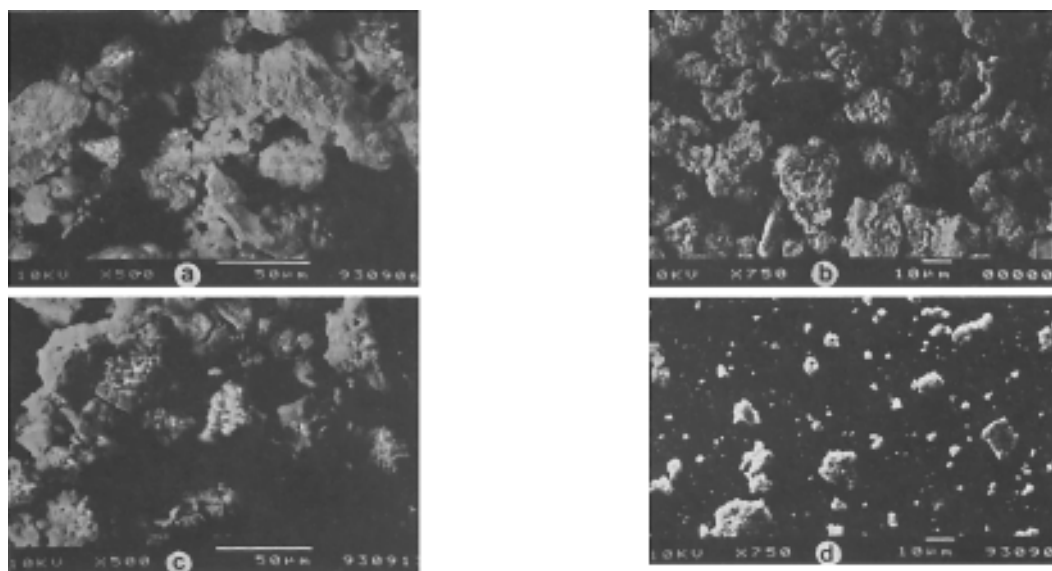
All resulting powdered silica gel samples were suspended in water/isopropanol (1:1, v/v). Photomicrographs were obtained with a scanning electron microscope (Jeol JSM 330 A).

## Results and Discussion

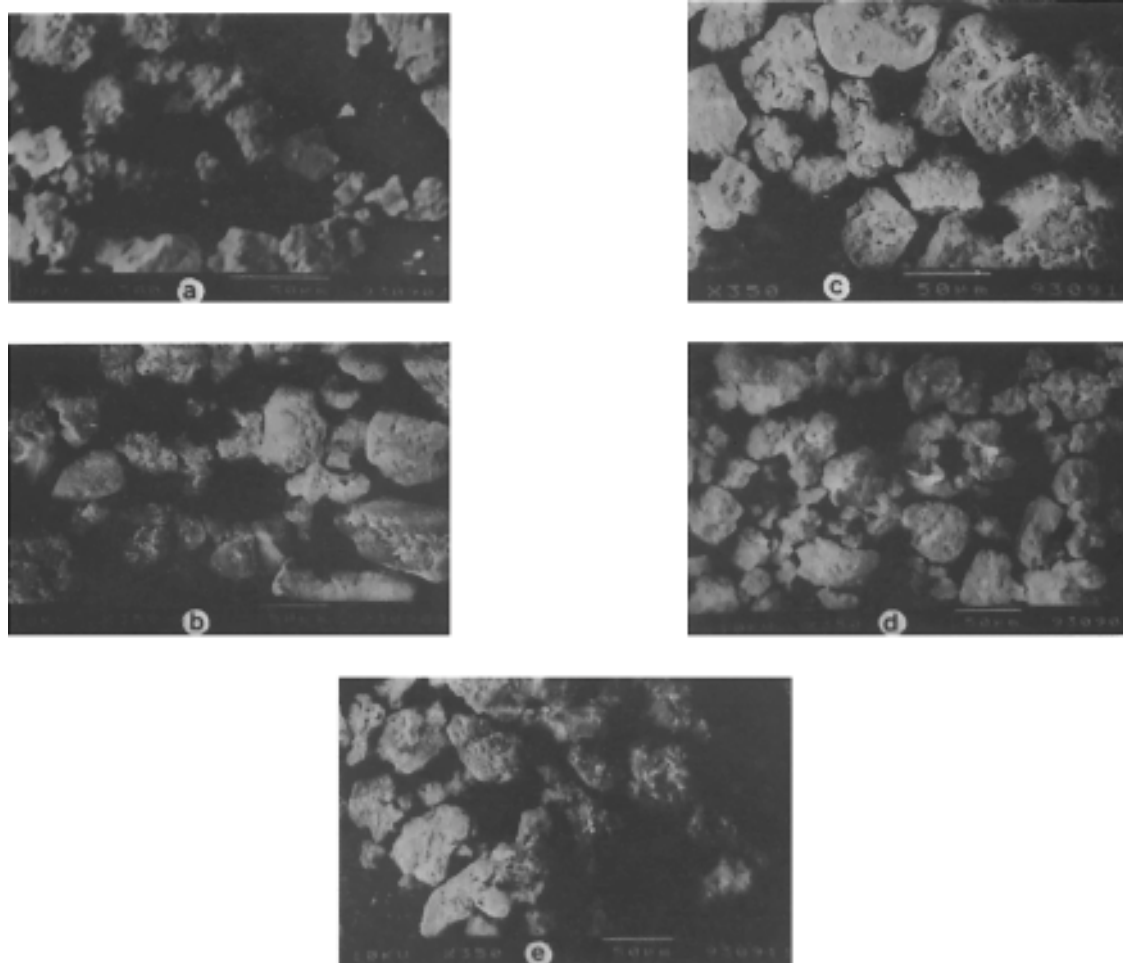
The silica photomicrographs are shown in Figs. 1, 2 and 3. Figure 1 shows the drying effect on samples without solvent treatment, and Fig. 2 shows the effects of different solvents using the vacuum desiccator in the drying process. In Fig. 3, the effects of propanone and ethanol are illustrated, as well as the effects of the drying process.

As illustrated in Fig. 1, silica gel samples, without any previous treatment, dried in a microwave oven (a) or in a vacuum desiccator (c) exhibit a smoother aggregate surface than samples dried in the drying oven (b) or in the freeze drier (d). This smooth surface is explained by the migration of fine particles and their coalescence on the surface, driven by different drying mechanisms. In the microwave oven process, the heating is due to the interaction of the radiation with the polar solvent<sup>8</sup> to the equally in the bulk or on the surface. In this process, the solvent activation energy can cause aggregate collapse. However, as the microwave radiation interacts with silica particles, the silanol groups can form polycondensation products and this can give a smoother surface. In the drying process the microwave oven leads to a greater change in the particle morphology. In the vacuum desiccator drying process, the driving force is the high water surface tension, which provides capillary forces based on the Gibbs-Kelvin equation which relates solvent vapor pressure to silica fine particle curvature and pore geometry. The time for water elimination in the vacuum desiccator is long enough to improve coarsening. The particle coalescence in these processes probably occurs due to fine particle coarsening, which is a dissolution and reprecipitation process during drying<sup>5</sup> that is driven by the differential solubility of the fine particles.

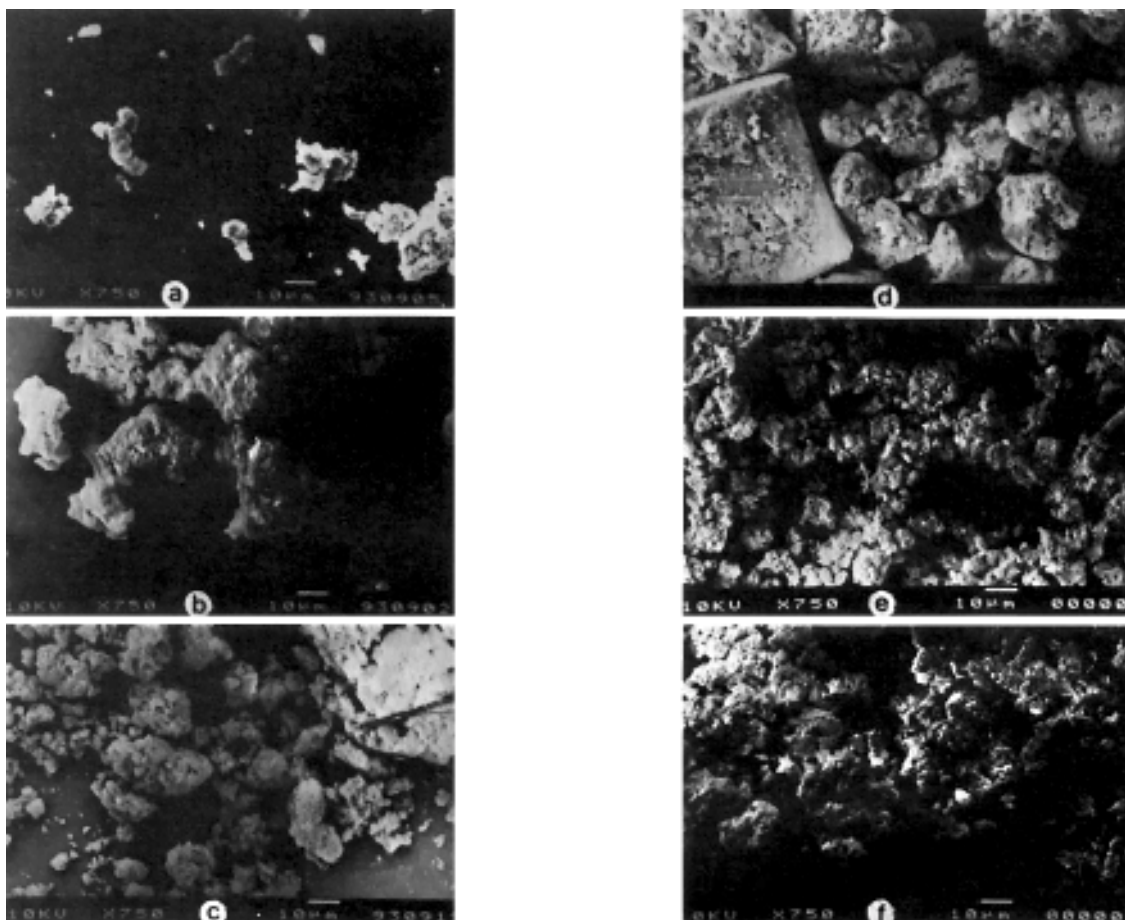
The sample dried in the drying oven (Fig. 1b) shows a higher surface roughness (porosity). This can be explained by the higher evaporation rate that takes place on the surface compared to the bulk of particles, causing shrinkage of the aggregate.



**Figure 1.** Photomicrographs of silica gels without treatment and dried by different processes: (a) microwave oven, (b) drying oven (100 °C), (c) vacuum desiccator, and (d) freeze drier.



**Figure 2.** Photomicrographs of silica gels treated with different solvents and dried in a vacuum desiccator: (a) water, (b) ethanol, (c) methanol, (d) propanone, and (e) ethyl ether.



**Figure 3.** Photomicrographs of silica gels treated with different solvents and dried by different processes: (a) propanone/microwave, (b) ethanol/microwave, (c) propanone/drying oven, (d) ethanol/drying oven, (e) propanone/freeze drying, and (f) ethanol/freeze drying. The results of drying in the vacuum desiccator are shown in Fig. 2, (d) and (b).

Freeze dried particles and aggregates (Fig. 1d) were frozen at  $-20\text{ }^{\circ}\text{C}$  and then slowly heated under low pressure (*ca.* 1 mmHg) so as to retain their structural features. This allowed for a low evaporation rate followed by small particle migration and adsorption on the aggregate surface, leading to either no coarsening or a low coarsening.

The drying process in the vacuum desiccator is slower and less disruptive than the other ones, and the results from it were chosen to illustrate the effect of solvents on morphology. It is generally accepted that the silica gel surface structure consists of silanol groups and siloxane linkages that strongly interact with polar molecules. Ethyl ether molecules do not wet the hydrophilic silica particle surface due to their low interaction with silanol and siloxane groups. Moreover, particles aggregate in this solvent resulting in silica similar to that which has not undergone any solvent treatment but has been dried in the same manner (Figs. 2e and 1c).

Other polar solvents (water, propanone, methanol and ethanol) have an affinity for silanol groups. However, it seems that they have different effects on the particle sur-

face, because the presence of solvents allows for preferential anchoring in silanol groups. It is widely accepted that water molecules interact strongly with silanol groups. In Fig. 2 it can be observed that aggregate roughness decreases in the order: propanone > methanol > ethanol > water. This sequence is in agreement with the increase in the boiling points of the solvents (propanone,  $56.2\text{ }^{\circ}\text{C}$ ; methanol,  $65.15\text{ }^{\circ}\text{C}$ ; ethanol,  $78.5\text{ }^{\circ}\text{C}$ ; and water,  $100\text{ }^{\circ}\text{C}$ )<sup>9</sup>. According to the Gibbs-Kelvin equation, particle solubility is an exponential function of interfacial tension. Also, solvent vapor pressure inside the pores depends on the pore radius. Increasing solvent surface tension (methanol,  $22.61\text{ mN m}^{-1}$ ; ethanol,  $22.75\text{ mN m}^{-1}$ ; propanone,  $23.70\text{ mN m}^{-1}$ ; and water,  $72.75\text{ mN m}^{-1}$ )<sup>9</sup> probably causes the fine particles to move to the surface. These data imply that water and propanone are the most effective solvents in the drying process for silica gel. In addition, contact time between solvent and finer particles on the surface is important for coarsening. In this step, the boiling points (vapor pressures) play an important role. The lower the solvent vapor pressure, the higher is the solvent-particle contact time, allow-

ing for coarsening and providing a smoother aggregate surface. Among these solvents, water has the highest surface tension and boiling point, so it is the solvent that provides the greatest coarsening. In contrast, propanone with moderate surface tension provides high enough capillary forces that the fine particles move out to the surface, while its low boiling point leads to the fastest evaporation rate, which eliminates coarsening.

Coarsening of fine particles is also observed by comparing the results of solvent treatments with propanone and ethanol with different drying process, in Fig. 3. All samples, especially those dried in the microwave oven or drying oven, presented smoother surfaces when treated with ethanol than when treated with propanone.

### Conclusions

Silica gel obtained from sodium silicate by the addition of HCl, washed and without other solvent treatment, undergoes the most extensive morphological change when dried in the microwave oven. However, the freeze drying process retains the features of the original sample. The former breaks down the gel structure due to the microwave effect on the polar solvent of the bulk particles. The latter is a less disruptive process of solvent withdrawal without changing the gel structure.

The solvent treatment effect on silica prepared in this concentration is not important for determining aggregate shapes, but it is significant in determining surface roughness. Water is the solvent that causes the greatest surface smoothing while propanone leads to aggregate roughness. This effect is mainly related to particle solubility, which is a function of solvent surface tension and particle radius, as

well as to the boiling point, which determines the contact time between particle and solvent.

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