

## Short Communication

# Structural inhomogeneities in wide-pore silica gels

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### Abstract

The cause of a bimodal or multimodal pore-size distribution in wide-pore silica gels made by a calcination procedure were elucidated. It was found that the process of crystallization of salt out of the pores of the silica gel is influenced by the nature of the salt and by the rate of evaporation of water. If these parameters were optimized, the pore structure of wide-pore silica gel prepared by this method was more uniform and the batch-to-batch repeatability of the process was greatly improved.

### 1. Introduction

Silica gels still dominate HPLC applications and include macroporous and even gigaporous (wide-pore) particles with pore diameters of 10–100 nm and >100 nm, respectively. The most common applications are size-exclusion chromatography [1] and procedures in which the chromatographic functions are attached to macromolecules accommodated within the pores of carriers [2–9].

Wide-pore silica gels can be prepared by the controlled polycondensation of silicic acid, but the maximum pore size so far prepared in this direct way hardly exceeds 100 nm [10]. A more efficient way to prepare wide-pore silica gel is the indirect route, *e.g.*, by enlarging the pores of readily available mesoporous materials [11–15].

Tanaka *et al.* [16] investigated microscopically the texture of various commercial silica gels. They found that wide-pore silica gels ( $D = 30\text{--}400$  nm) usually possessed pores of two or even

several different sizes within the same sample. This resulted in wide or bimodal pore-size distribution curves of the silica gels as measured by different methods. The logical conclusion of Tanaka *et al.* [16] was that the samples studied were in fact mixtures of at least two different materials.

In this study, we tried to answer the question of whether such mixtures can be formed unintentionally in the course of wide-pore silica gel production and, if so, what the cause of these irregularities is and how they can be prevented.

### 2. Experimental

Scanning electron microscopy was carried out with a Jeol 35 SEM.

#### 2.1. Silica gel

An experimental sample (SG-10) was prepared in this Institute with surface area, pore volume and particle diameter of  $320\text{ m}^2\text{ g}^{-1}$ , 1.8

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$\text{cm}^3 \text{g}^{-1}$  and 8–12  $\mu\text{m}$ , respectively. Silica gel LiChrospher Si-100 (10  $\mu\text{m}$ ) was obtained from Merck (Darmstadt, Germany).

### 2.2. Preparation of wide-pore silica gel

A 25% aqueous solution of a suitable salt, typically NaCl, was slowly added to carefully stirred silica gel in a glass beaker to form only slightly wet material. This means that almost the whole volume of solution was soaked up by the pores of the silica gel. The mixture was transferred into an oven and dried at different temperatures above 110°C and under different arrangements. The dried materials were heated in a furnace at different temperatures and for different durations, typically at 700°C for 2 h. The salt was then leached out with an excess of distilled water and the remaining silica gel was dried after washing.

### 3. Results and discussion

We applied a calcination procedure for widening the pore size of conventional (6–20-nm) silica gels as introduced by Krebs and Heintz [17], as this method or its modifications are probably used by the producers of commercial wide-pore silica gels. It is based on filling the pores of silica gel with a neutral, thermostable inorganic salt with melting point above 300°C and calcinating the composite. At high temperatures, both the silica gel and the salt at least partially liquefy and phase separation occurs. The size and shape of the phases formed depend on the amount and nature of the salt and on the conditions of calcination. The phases solidify when the temperature drops and, subsequently, the salt phase is leached out, leaving wide-pore silica gel with pore diameters of  $\geq 1000$  nm.

Using the Krebs and Heintz method [17], we produced with a single procedure and from the same starting bimodal, “mixed” materials as reported by Tanaka *et al.* [16] (Figs. 1 and 2). Careful investigation of single particles of silica gels by scanning electron microscopy showed that the bimodal pore structure may be

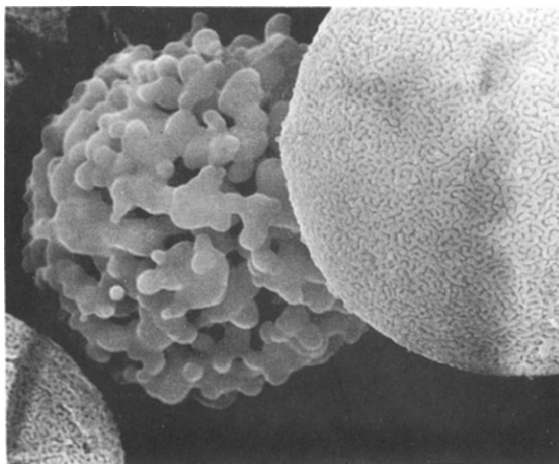


Fig. 1. Scanning electron micrograph of silica gel SG-10 soaked and dried with salt, heated at 800°C for 30 min, washed out with water and dried.

present even within single particles (Figs. 3 and 4). Sometimes, the particles contain shell or skin regions (Fig. 5). On the other hand, the regular sponge-like structure of wide-pore silica gels prepared by the Krebs and Heintz method [17] typically has a very narrow pore-size distribution (Fig. 6). This means that wide-pore silica gels prepared by the calcination method may inherently consist of mixtures of materials with different pore sizes, each possessing a narrow size distribution.

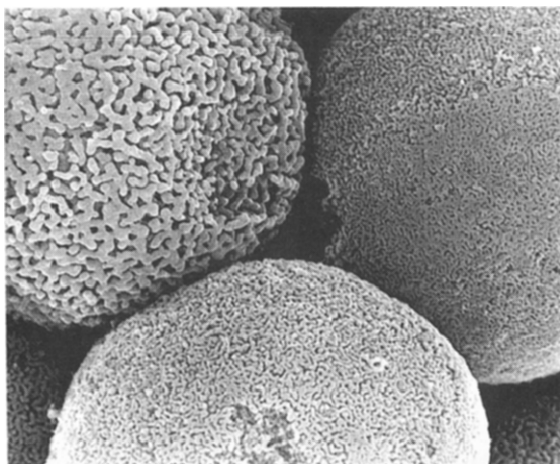


Fig. 2. Scanning electron micrograph of silica gel SG-10. Treatment as in Fig. 1.

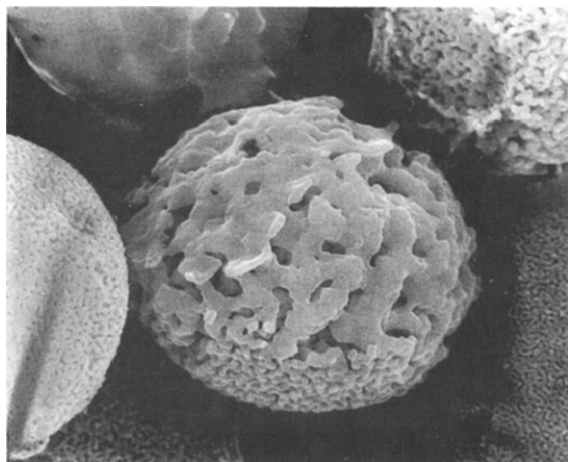


Fig. 3. Scanning electron micrograph of silica gel SG-10 soaked and dried with salt, heated at 700°C for 1 h, washed out with water and dried.

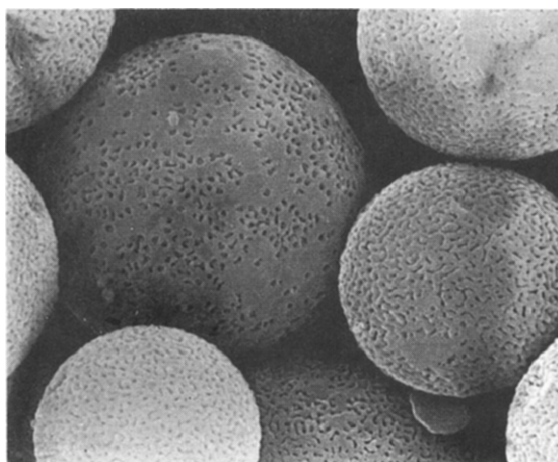


Fig. 5. Scanning electron micrograph of silica gel LiChrospher Si-100 treated with salt, heated at 700°C for 2 h, washed out with water and dried.

In order to explain the reasons for bimodal and multimodal structure formation, we also checked microscopically the raw material and the intermediate products formed under different experimental conditions. We found that a voluminous phase of fine wool-like crystals was formed on the surface of the layer of material during drying (Fig. 7) and in this instance the final silica gel possessed a bi- or multimodal pore structure. This means that during calcination

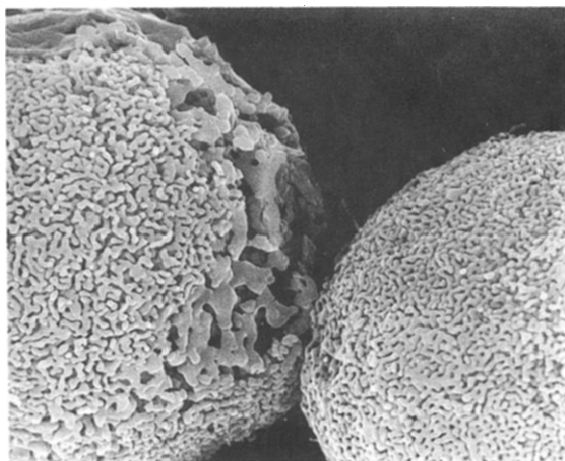


Fig. 4. Scanning electron micrograph of LiChrospher Si-100 treated with NaCl, heated at 750°C for 2 h, washed out with water and dried.

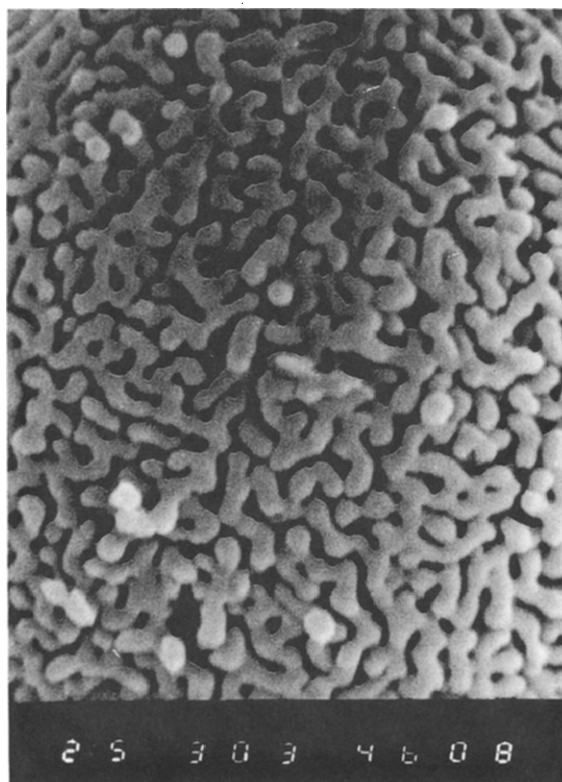


Fig. 6. Scanning electron micrograph of LiChrospher Si-100 soaked in NaCl solution and dried, heated at 800°C for 1 h, washed out with water and dried.

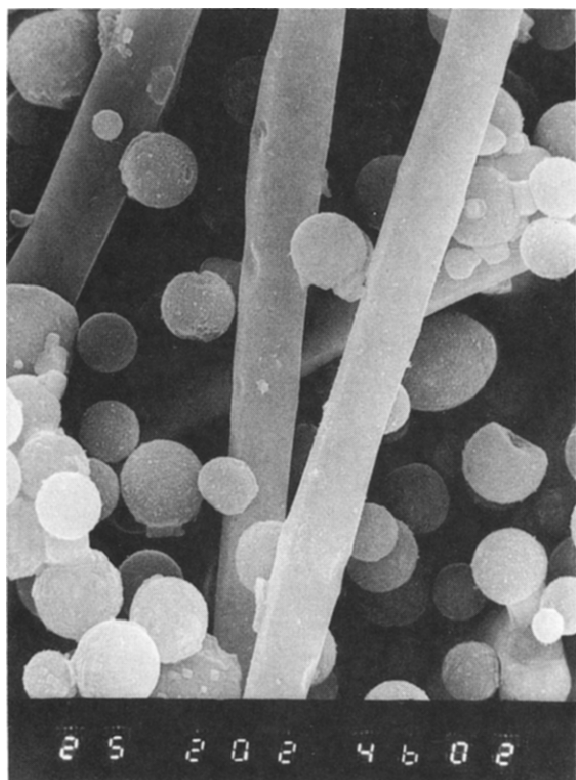


Fig. 7. Scanning electron micrograph of silica gel SG-10 after drying with the salt.

some pores were empty whereas others were filled only partly with salt, and only a small fraction of the pores was optimally saturated with salt. This could explain why pores with different structures are formed within one batch of silica gel or even within a single particle.

A possibility for improving the uniformity of wide-pore silica gel prepared by the calcination method is the cautious stirring of either the silica during water evaporation or dry silica gel con-

taining crystals of salt so that the long needles are broken. In any event, the resulting dry mixture must be as homogeneous as possible so that salt melted during calcination can more easily re-enter the pores of the silica and the phase separation can proceed homogeneously.

#### 4. References

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