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PREPARATION OF POROUS SILICA SPHERES FOR COLUMN LIQUID CHROMATOGRAPHY

KLAUS UNGER and JURGEN SCHICK-KALB

Technische Hochschule, 61 Darmstadt (G.F.R.)

and

KARL-FRIEDRICH KREBS

Fa. E. Merck, 61 Darmstadt (G.F.R.)

SUMMARY

A new procedure for the preparation of porous silica spheres is described, which enables very small particles with a narrow size range to be prepared. Furthermore, the parameters of the pore structure can easily be controlled by the reaction conditions. In this way, porous silica supports of high efficiency were developed for the different types of liquid chromatography.

INTRODUCTION

The development of supports of high efficiency is one of the most important problems in liquid chromatography. The column efficiency can be much improved by decreasing the particle size of the porous support, and as a result special types of porous silica have been developed with a mean particle diameter $d_p \leqslant 10 \, \mu\text{m}$ (ref. 1). However, these supports should also have a definite pore structure, which depends on the type of liquid chromatography (partition, adsorption, ion-exchange or gel permeation) being considered.

Firstly, the porous silica should be available with graduated values of the average pore diameter and the specific surface area. Supports for partition and gel permeation chromatography should exhibit a high specific pore volume at a homogeneous pore size distribution.

On the other hand, the development of highly porous silica leads to the possibility of improving the column performance. As stated above, the diffusion path length of solute molecules can be shortened by using very small particles. However, the mean particle diameter of the porous support is limited to a value of about 5 μm, because it is very difficult to pack such columns with good reproducibility. In order to increase the accessibility of the pores of the small particles, supports should be synthesized with a high specific macropore volume. The macropores should be distributed on the surface of the particles as large holes and should have pore widths

ten times smaller than the particle diameter (1000–5000 Å). Furthermore, these macro-pores should also be the entrances to the smaller pores (intermediate pores).

In order to attain all these requirements for a special pore structure, a new procedure of preparing porous silica was developed, which was based on the earlier investigations of Kohlschütter and Mihm[2]. The procedure and the dependence of pore structure on the reaction conditions will be published in detail elsewhere[3]. This paper deals with the results, which are interesting for the development of silica supports of high efficiency for column liquid chromatography.

EXPERIMENTAL

A general description of the preparation procedure is given below.

The formation of porous silica consists of two stages. In the first stage, a viscous liquid polyethoxysiloxane is prepared by partial hydrolysis of tetraethoxy-silane, and in the second step (Fig. 1) the polyethoxysiloxane is emulsified with a mix-ture of water and ethanol. After emulsification by stirring, a catalyst is added, which initiates the hydrolytic polycondensation of the drops of polyethoxysiloxane to yield solid spheres of silica hydrogel. The hydrogel is separated from the solution and de-hydrated to yield porous silica. By varying the mean molecular weight of the poly-ethoxysiloxane and the reaction conditions (e.g., the type of catalyst, the catalyst concentration, the temperature, the relative proportions in the ethanol–water mixture) the parameters of the pore structure can be influenced and controlled.
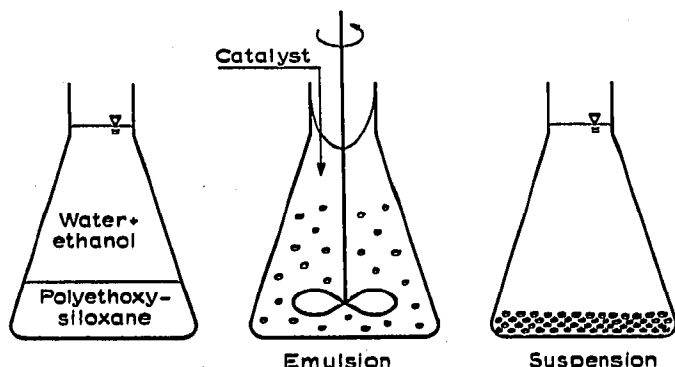

Fig. 1. Scheme of the procedure for the preparation of porous silica spheres.

RESULTS AND DISCUSSION

Particle size and particle size range

The particle size range can easily be controlled by means of the stirring speed during the hydrolytic polycondensation of the polyethoxysiloxane. Fig. 2 shows the effect of the stirring speed on the particle size distribution. In this simple way, porous silica spheres with graduated average particle diameters and relatively narrow size ranges can be prepared. By subsequent sedimentation or sieving, very narrow cuts of particle size ranges are obtained. The spherical shape of the porous particles permits the reproducible packing of the columns.
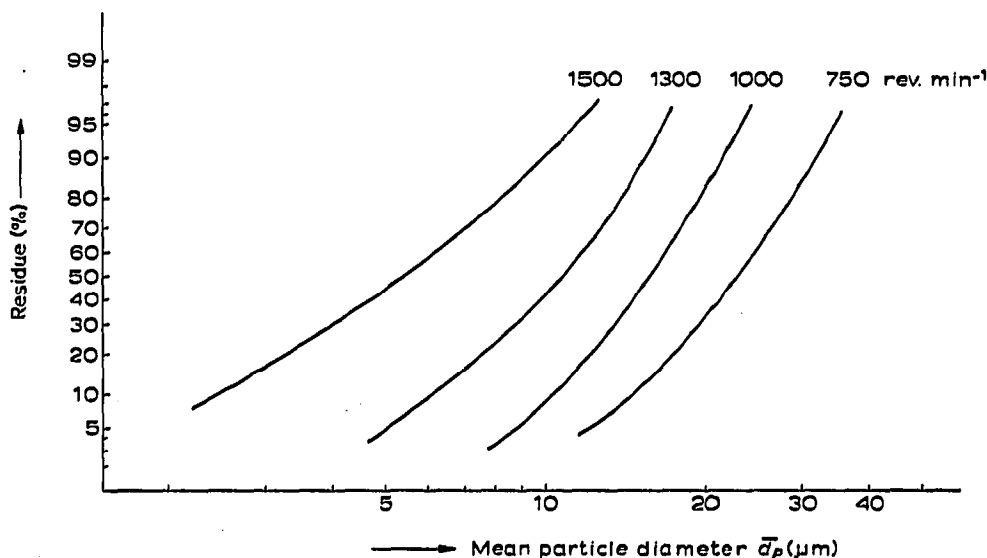
Fig. 2. Effect of the stirring speed on the particle size distribution.

Average pore diameter

The average pore diameter of the porous silica spheres can be controlled in the range between 30 and 300 Å by means of the catalyst concentration in the second stage of the preparation procedure. Table I shows the properties of a series of silica samples in which the catalyst concentration was varied. With increasing catalyst concentration, the specific surface area decreases and the mean pore diameter increases. The products show a homogeneous pore size distribution. A maximum specific pore volume of 1.5 ml g^{-1} was attained. These products were used as supports for adsorption and partition chromatography[4].

Supports with larger pores (mean pore diameter $\bar{D}$ > 300 Å) were favourably prepared by the special treatment of the porous particles with a solution of NaCl and calcination of the salt-loaded gel at higher temperatures[5]. Fig. 3 shows the integral pore size distribution curves of products that were treated by the "salt method". The starting material for all samples was silica No. 5 in Table I. The average pore diameter can be varied in the range between 400 and 30,000 Å (the maximum value

TABLE I

PROPERTIES OF POROUS SILICA SAMPLES WITH INTERMEDIATE PORES USED AS SUPPORTS FOR ADSORPTION CHROMATOGRAPHY

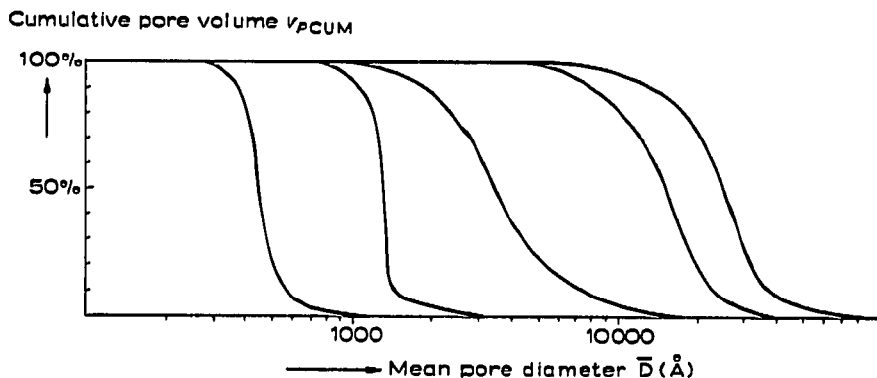| No.	Specific surface area, s_{BET} (m^2 g^{-1})	Specific pore volume, v_P (ml g^{-1})	Mean pore diameter, $\bar{D}$ (Å)
1	540	0.57	30
2	464	0.63	40
3	412	0.76	50
4	334	0.88	60
5	310	0.90	80
6	270	1.18	140

Cumulative pore volume v_{PCUM}

Fig. 3. Integral pore size distribution curves of porous silica spheres, determined by the mercury intrusion technique.

of 30,000 Å was obtained by using porous particles with an average particle diameter of about 100 μm). By varying the treatment conditions, not only the average pore diameter but also the steepness of the integral pore size distribution can be controlled. Furthermore, the products exhibit a relatively large specific pore volume in the range between 0.7 and 1.0 ml g^{-1}. These products are excellent supports for partition and gel permeation chromatography[6].

Specific pore volume and porosity

A special effect on pore structure is obtained by adding a solvent such as cyclohexane to the polyethoxysiloxane in the second step of the preparation procedure (Fig. 1) before starting the hydrolytic polycondensation.

Because the formation of the spheres of the silica hydrogel occurs very rapidly, the added solvent is almost completely included in the solid particles. This mode of preparation yields a product with a higher specific pore volume than that without a solvent. Consequently, the specific pore volume of the porous spheres is a linear function of the amount of solvent added. In this way, we prepared samples with graduated values of the specific pore volume up to a maximum of about 4.0 ml g^{-1}. From the results on the pore size distribution, we can conclude that the additional amount of the specific pore volume is due to larger intermediate pores (300 $< \bar{D} <$ 2000 Å) and to macropores ($\bar{D} >$ 2000 Å).

Two different specifications of the procedure are possible, yielding two kinds of products:

(1) products with a nearly constant specific pore volume and graduated specific surface areas in the range between 200 and 500 m^2 g^{-1};

(2) products with a nearly constant specific surface area and graduated specific pore volumes in the range between 1.0 and 4.0 ml g^{-1}.

Table II shows the properties of products that have nearly constant surface areas and graduated values of the specific pore volume. Sample 1 was obtained without adding cyclohexane. It has an average pore diameter of about 150 Å and a homogeneous and symmetrical pore size distribution. Samples 2-5 were prepared by adding an increasing amount of cyclohexane. The samples show an unsymmetrical pore

TABLE II

PROPERTIES OF POROUS SILICA SAMPLES WITH GRADUATED VALUES OF POROSITY

No.	Specific surface area, s_{BET} $(m^2 g^{-1})$	Specific pore volume, v_P $(ml g^{-1})$	Porosity P $(\%)$
1	270	0.97	66.0
2	240	1.40	74.0
3	217	1.79	79.0
4	220	2.20	82.0
5	210	4.12	90.0

size distribution. In the sequence of samples 2–5, the macropore volume increases, whereas the specific pore volume of the intermediate pores remains constant. The intermediate pores are mainly responsible for the value of the specific surface area and are accessible by the macropores.

Using the products in Table II, we can investigate the effect of the accessibility of pores on the column efficiency in adsorption and partition chromatography.

CONCLUSION

The objective of this paper has been to show the variability of the pore structure of porous silica spheres with respect to the development of supports of high efficiency for column liquid chromatography.

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