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Toroidal microporous silica gel

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Microporous amorphous silica gel with a characteristic toroidal form of the elementary particles, has been prepared by thermal dissociation of a solution of silicic acid in a spray dryer. The substance obtained was investigated by electron microscopy, infra-red spectroscopy and thermal analysis. The adsorption properties were studied by low-temperature adsorption of nitrogen.

1. Introduction

There are more than 100 kinds of polycondensation products of silicic acid which are generally produced under the name of "silica gel" [1]. However, their main characteristics such as form, size and volume of the pores, grain size, specific surface area, etc., show considerable differences. The physico-chemical properties of silica gel depend on the method of its preparation and additional treatment [2, 3]. Investigations are being carried out aiming at the preparation of new kinds of silica gel. In most cases the researchers are interested in the effect of the conditions of preparation on the above parameters.

The particle forms of finely dispersed amorphous silica gel can play an important role. However, this problem has not been studied enough up to now. In the present paper, a method for the preparation of finely dispersed amorphous silica gel with toroidal particles is described and the results obtained on the properties of this silica gel are presented.

2. Experimental details

A solution of water-glass (5%) was passed through a column containing cation exchange resin in the hydrogen form. The sodium of the silicate was replaced by a hydrogen ion and the obtained solution of silicic acid was introduced into a spray dryer where, at a temperature of 250° C, powdery silica gel was prepared [4] and subjected to adsorption measurements. The adsorption isotherm of nitrogen was obtained at 77.4 K under relative pressures ranging from 0 to 1 P/P_0. The electron micrographs were made with JEM 100 B, and the infra-red spectra were recorded by UR-20. DTA curves were registered with a derivatograph.

3. Results and discussion

3.1. Electron-microscope study

The microhabit of the silica gel particles is shown in Figs. 1 to 3 at different magnifications. The particles have regular shapes and smooth surfaces. Their formation is due to the effect of the silicic acid solution in the spray dryer where the processes take place at a high rate. On reaching the dryer, the solution is dispersed into fine drops which begin to rotate. With increasing concentration, the silicic acid is polymerized and a gel is formed. The silicon tetrahedra are arranged toroidally. Heating to 250° C accelerates the dehydration of the plastic gel leading to the formation of a solid porous xerogel and its partial dehydration. The number of siloxane bonds increases and the porous structure of the gel particles becomes stable.

3.2. Thermal study

No thermal effects are observed on the DTA and DTG curves within the temperature range 300 to

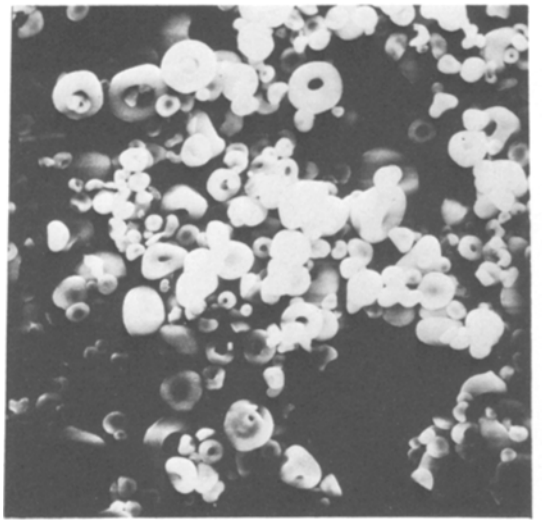

Figure 1 Scanning electron micrograph of toroidal microporous silica gel, × 1640.

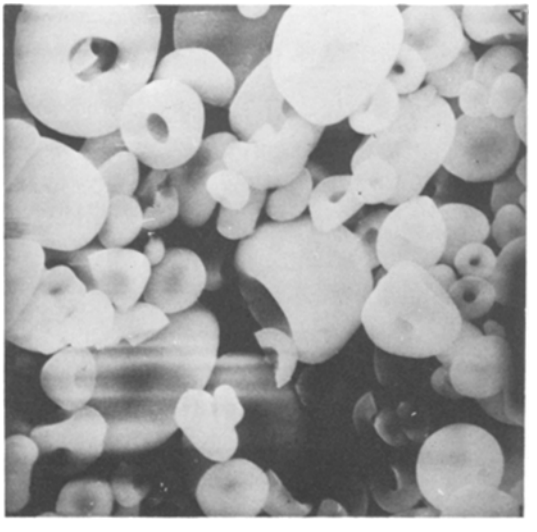

Figure 2 Scanning electron micrograph of toroidal microporous silica gel, × 5800.

600° C (Fig. 4). On removal of the physically adsorbed water at 100 to 200° C, a second endothermal peak appears at 700 to 800° C where the actual dehydration takes place, 5.5% of the water being removed. The number of OH groups corresponding to a surface area of 100 Å, calculated by the formula of Vleeskens [5], is 13 to 14.

3.3. Infra-red spectroscopy

The most pronounced peak in the infra-red spectrum of the substance obtained is that corresponding to deformations caused by OH groups at

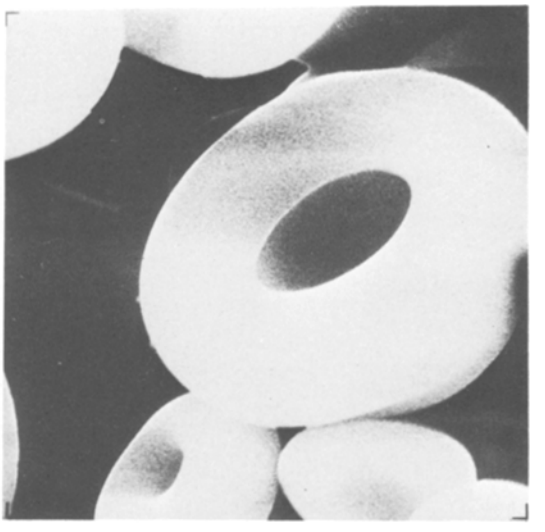

Figure 3 Scanning electron micrograph of toroidal microporous silica gel, × 11 600.

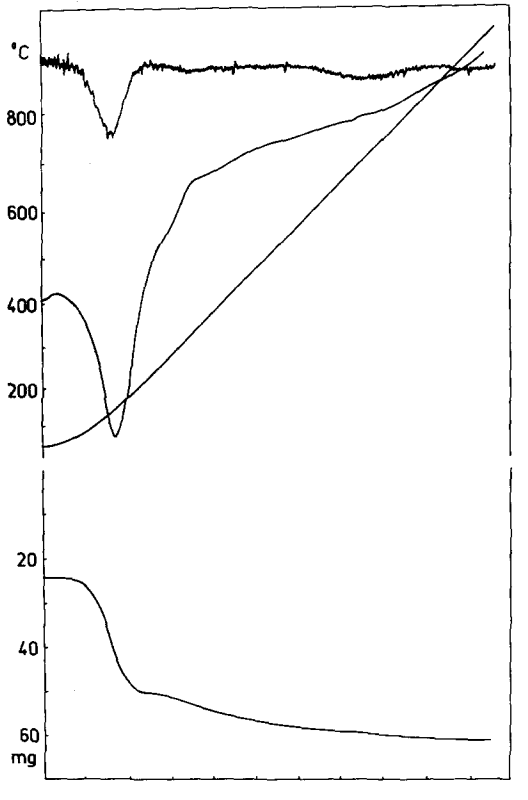

Figure 4 Thermogram of toroidal microporous silica gel. Apparatus: derivatograph; heating rate: 10° C min^{-1}.

1100 cm^{-1} (Fig. 5). The peak produced at 1640 cm^{-1} by adsorbed water is considerably lower. Since the peak of the valence fluctuations of the OH groups appears at 3440 cm^{-1}, it has to be assumed that the water is present in the sub-

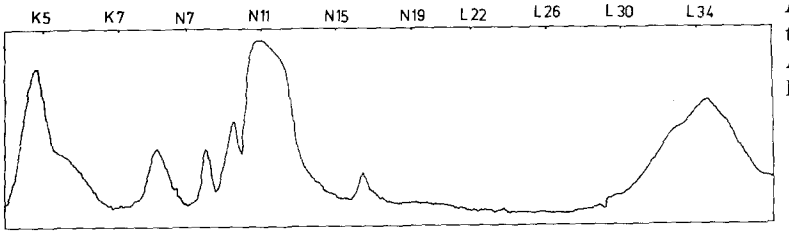

Figure 5 Infra-red spectrum of toroidal microporous silica gel. Apparatus: UR-20 (Zeiss, Jena); KBr tablet.

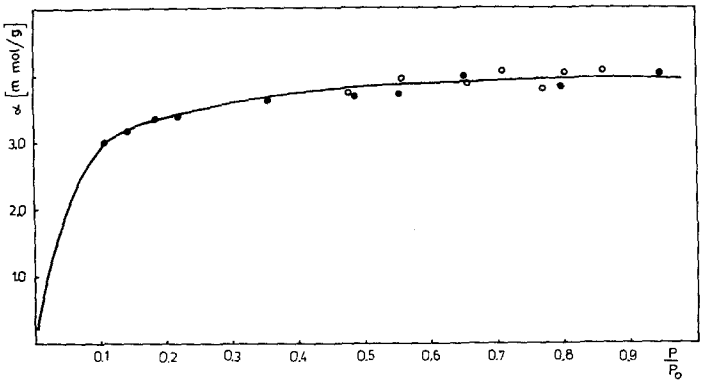

Figure 6 Adsorption isotherm of nitrogen on toroidal microporous silica gel at 77.4 K.

stance studied in the form of OH groups between which there are hydrogen bonds. The peaks at 800 and 400 cm^{-1} characterize the Si–O bonds.

3.4. Adsorption studies

The best way of characterizing the texture of silica gel is by studying its adsorption properties. Fig. 6 shows the adsorption isotherm of nitrogen at 77.4 K. As is evident, this is a Langmuir type isotherm (Type I) [6] and differs considerably from the usual curve shapes corresponding to amorphous silica gel which are of Type II. The adsorbed nitrogen amount quickly increases in the region of low relative pressures (0.1 to 0.2 P/P_0) and reaches its maximum value, which remains constant, in the range between 0.5 and 1.0 P/P_0. This type of adsorption isotherm corresponds to microporous adsorbents for which the adsorbed amount is restricted to several adsorption layers and is larger than the amount adsorbed by samples with large pores under the same relative pressures, due to the effect of the opposite faces which are situated close to each other. According to modern concepts [6], the shape of the adsorption isotherm at low relative pressures is due to this effect of the opposite faces, and the plateau of the adsorption isotherm corresponds to filling of the pores and not to a monolayer coverage. The pore size of this type of adsorbents varies from 4 to 15 Å. The BET method is not appropriate for the determination of the specific surface area, but there are still no accurate and reliable methods to that purpose [6]. In order to make an approximate estimation of the surface and to check the extent to which the adsorption isotherm corresponds to the Langmuir type, we wrote this isotherm as

$$P/V = 1/BV_m + 1/V_mP$$

where P is the pressure, V the adsorbed nitrogen in cm^3 at normal temperature and pressure (NTP), V_m denotes the volume (at NTP) of nitrogen needed for a monolayer coverage of the surface, and B is a constant. As is evident from Fig. 7, dependence P/V–P is linear. The specific surface area calculated from V_m is 402 $m^2 g^{-1}$. The high value obtained confirms the opinion expressed in [6] according to which the results obtained using this formula are higher than the real ones. However, this result shows that the pores are not narrowed and their total volume obtained by calculation corresponds to the real one. Taking into account this fact, the volume of the pores was calculated using the maximum adsorbed amount (the plateau of the adsorption isotherm), and the value of 0.138 $cm^3 g^{-1}$ was obtained. Therefore, the silica gel particles contain micropores whose total volume is small.

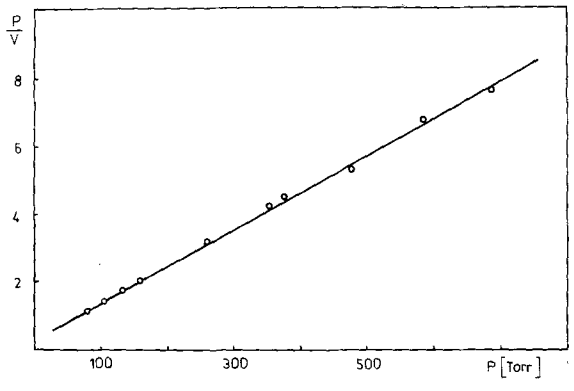

Figure 7 Dependence of P/V on P, calculated from the adsorption isotherm. P, pressure in Torr; V, adsorbed nitrogen in cm^3 at normal temperature and pressure (NTP).

4. Conclusions

Microporous amorphous silica gel with a toroidal form of the elementary particles has been obtained. It differs in its adsorption and physicochemical properties from the silica gel described in the literature. The apparatus used is very simple and the processes of precipitation, filtration and washing of the finely dispersed precipitate are eliminated.

References

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