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SURFACE AREA AND PORE STRUCTURE OF THERMALLY TREATED SILICA GEL

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ABSTRACT

Fine silica gel, prepared by grinding coarse granules to a particle size <100 μm, is heated in air at 100, 500, 600, 700, 800, 900, 1000, 1100, 1300, and 1400°C for 3 h. Pore structure is studied from variations in specific surface area, total pore volume and the mean hydraulic radii of the pore system available for nitrogen adsorption. These parameters are related as far as possible to changes in pore size, the distinct phases produced at each temperature, and the particle size of the crystallites as calculated from X-ray diffraction analysis.

INTRODUCTION

The structure of amorphous silica may be described as a coherent aggregate of small elementary particles [1]. The pore system located within the silica gel aggregate is formed by the open spaces between the elementary particles; electron micrographs provide direct evidence for this model [2]. Therefore, the high specific surface area of silica gel is approximately equivalent to the geometrical surface of the elementary particles in the structure [2,3].

Various types of silica may be obtained according to the methods and conditions of preparation [4,5]. The existence on silica surfaces of a distinct class of reactive hydroxyl groups has been reported [6]. Several investigators [7,8] postulated a relationship between silica pore diameter and the relative adsorption of various adsorbates; however, there is disagreement as to whether reduced pore diameter favours [9,10] or hinders [4,11—13] the adsorption of bulkier molecules.

Many investigations have been devoted to the study of hydrogen bonding between surface hydroxyl groups of silica and various adsorbed compounds [14—16]. Other studies revealed the occurrence of specific and non-specific intermolecular interactions [17—19] between the adsorbate molecules and silica surfaces; specific interactions predominate during adsorption of polar molecules and lead, for most microporous silicas, to unreliable values of surface area and pore volume.

In the present studies, nitrogen was used to investigate variation of pore structure of silica gel with treatment temperature, in order to try to eliminate specific interactions with the silica surface. The results obtained are related, as far as possible, to the distinct phases produced by the thermal treatment in each structure.

EXPERIMENTAL

A coarse silica gel (BDH) was ground to a particle size <100 μm diameter. These fine particles of silica gel were divided into 10 portions, each being heated in air at 100, 500, 600, 700, 800, 900, 1000, 1100, 1300, or 1400°C. The resulting samples are designated as SG100, SG500, SG600, SG700, SG800, SG900, SG1000, SG1100, SG1300, and SG1400, respectively.

Adsorption isotherms of nitrogen, at liquid nitrogen temperature, were determined volumetrically using a BET apparatus of the conventional type. Each sample was outgassed at 100°C for 1 h before an adsorption run.

The phases produced by the thermal treatment of silica gel were identified by X-ray diffraction analysis.

RESULTS AND DISCUSSION

The adsorption—desorption isotherms of nitrogen on the various treated silica samples are shown in Fig. 1. All isotherms are characterized by being reversible at all ranges of relative pressure; they belong to type II of Brunauer's classification, with varying sigmoid characters reflecting a change in the pore structure with treatment temperature. From the adsorption isotherms, the V_l—t plots were constructed using the low-heat t values reported in the literature [20]. The plots are shown in Fig. 2.

Some surface characteristics of the thermally treated silica samples as measured from nitrogen adsorption are given in Table 1 and the parameters derived are shown in Fig. 3. These parameters are the total surface area, the total pore volume and the mean hydraulic radius of the pore system as measured by nitrogen molecules.

The results obtained indicate that the same characteristic isotherms are obtained for nitrogen adsorption on the samples heated at 100—500°C with a predominance of micropores; the average width of the total pore system is indicated by the hydraulic radius of 6.78—7.86 Å. The conservation of the pore system on heating silica gel from 100°C to 500°C is mainly due to the reversible process water loss—water re-uptake: it was found that the water loss on heating at certain temperatures below 500°C is regained on cooling the sample in air to ambient temperature.

Heating of silica gel at 600°C is accompanied by a decrease in the surface area; the total pore volume increases on heating from 500°C to 600°C. The decrease in surface area at 600°C is mainly attributed to the initial elimination of micropores and the creation of some mesopores; micropores have a greater surface/volume ratio than mesopores. These effects can be clearly

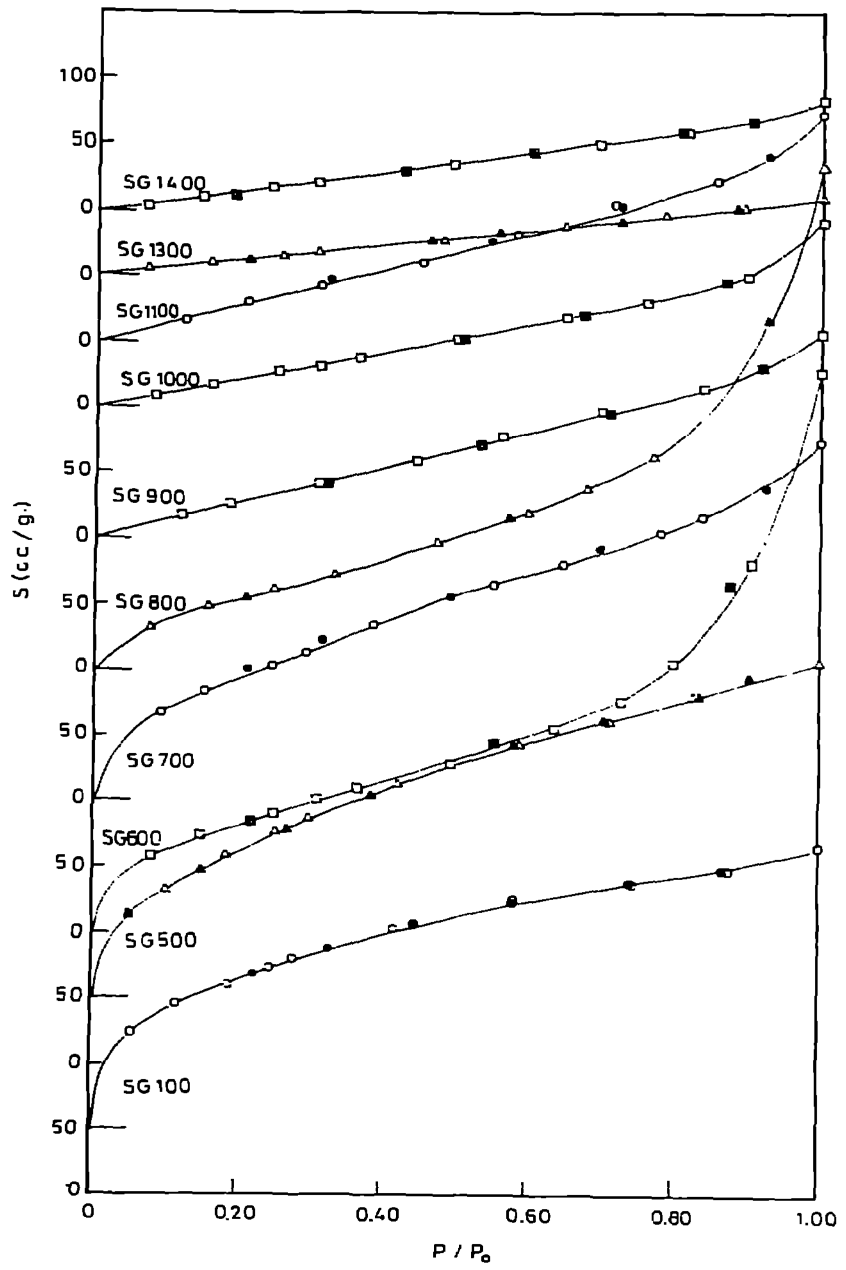

Fig. 1. Adsorption isotherms of nitrogen on the thermally treated silica gel.

understood from the strong downward deviation in the V_l—t plot obtained from the adsorption of nitrogen on the silica gel heated at 500° C; this downward deviation disappeared on heating the silica sample at 600° C, to be replaced by a minor upward deviation, showing the presence of some mesopores (cf. Fig. 2). All these variations resulted in an increase in average width of the total pore system (hydraulic radius) measured by nitrogen molecules (Fig. 3).

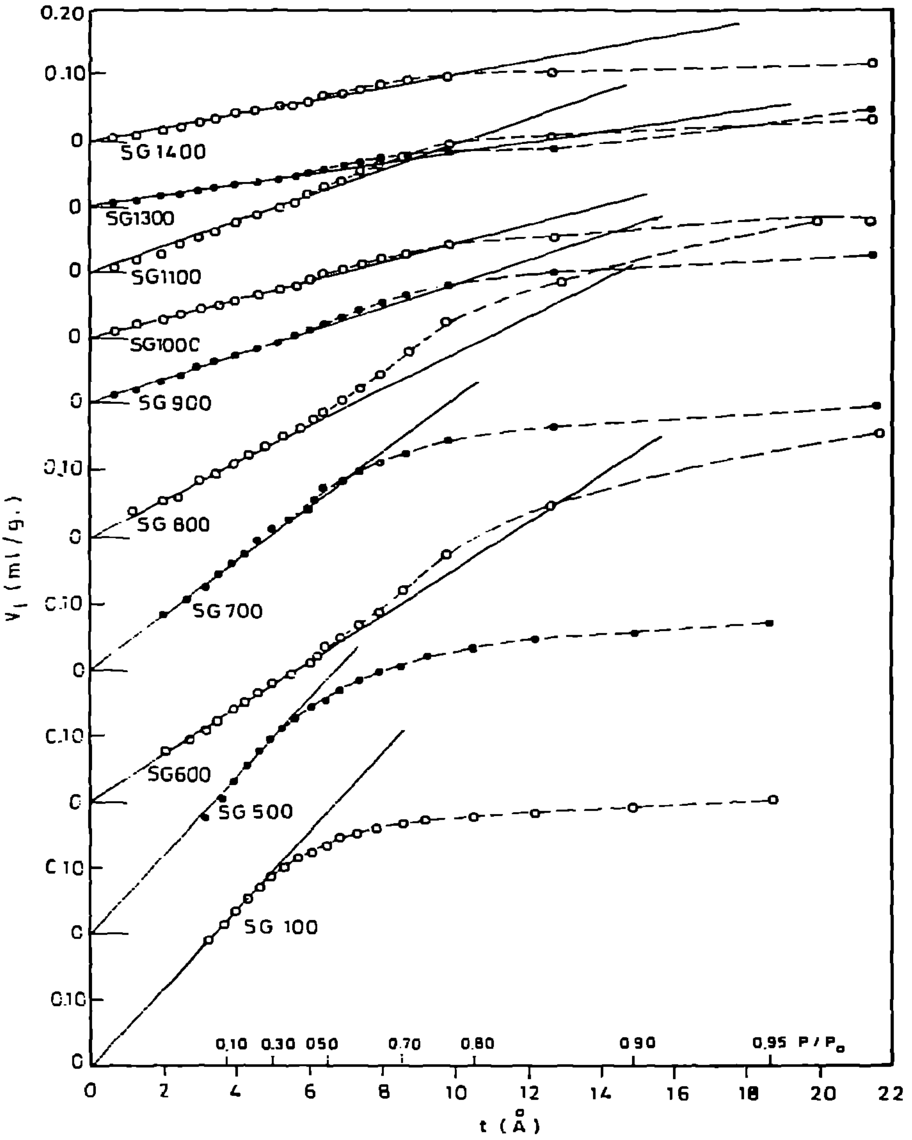

Fig. 2. V_l—t plots for the adsorption of nitrogen on the thermally treated silica gel.

Other groups of micropores, having a hydraulic radius of 10.87 Å, appeared after heating the silica gel at 700° C and this is accompanied by a reduction in the total pore volume and an increase in the surface area, as shown in Fig. 3; the V_l—t plot also demonstrated the existence of these micropores in the sample heated at 700° C (see Fig. 2). However, heating at 800° C is associated with a marked increase in the total pore volume; meanwhile the surface area decreased, because a large fraction of the total pore system is mesopores. This effect is indicated by increase in the hydraulic radius of the pore system (Fig. 3) and the upward deviation in the V_l—t plot (Fig. 2).

The results of X-ray diffraction analysis showed that no phase was

TABLE 1

Variation of nitrogen surface area, S_{BET}, total pore volume, V_p, and hydraulic radius, r_h, of the thermally treated silica samples

Sample	S_{BET} ($m^2\ g^{-1}$)	V_p ($ml\ g^{-1}$)	r_h (Å)
SG100	614.0	0.4162	6.78
SG500	614.0	0.4827	7.86
SG600	329.5	0.6695	20.32
SG700	394.5	0.4289	10.87
SG800	249.1	0.6006	24.12
SG900	213.7	0.2465	11.53
SG1000	154.0	0.2262	14.69
SG1100	235.6	0.2717	11.53
SG1300	104.5	0.0995	9.14
SG1400	137.5	0.1287	9.36

detected on heating silica gel to 700 or 800° C; this was attributed to conversion of the silanol groups into siloxane bridges (Fig. 4). The destruction of silanol groups is accompanied by a minor increase in particle size from 500° C to 800° C (see Fig. 5).

In the temperature range 900—1400° C, the V_l—t plots demonstrate the existence of mesopores with limited size (Fig. 2). The presence of these pores in this temperature range reflects parallel changes in the surface area and the total pore volume with treatment temperature (Fig. 3). X-Ray dif-

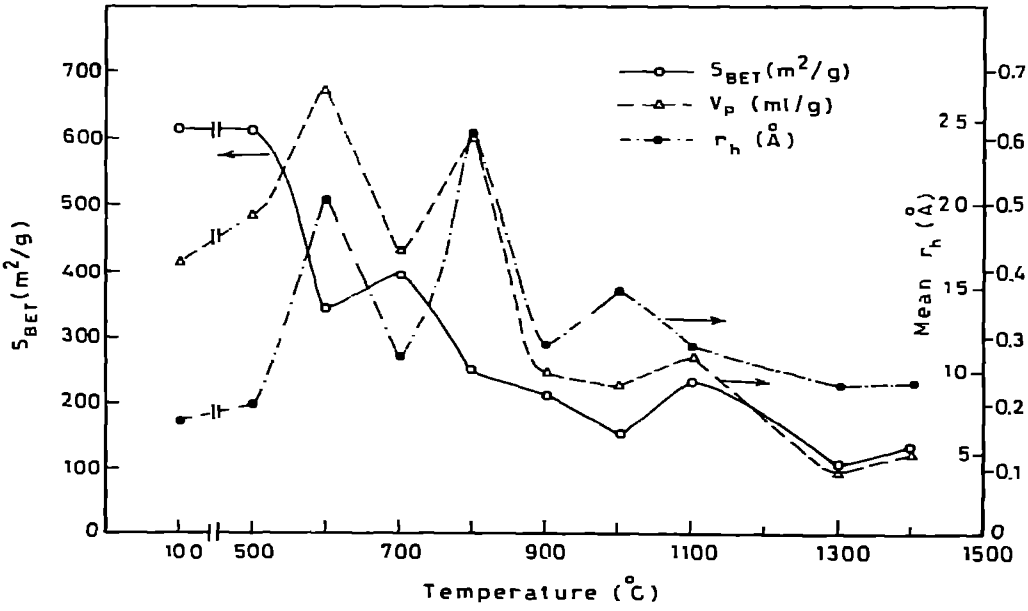

Fig. 3. Variation of nitrogen surface area, total pore volume and hydraulic radius with pretreatment temperature of silica gel.

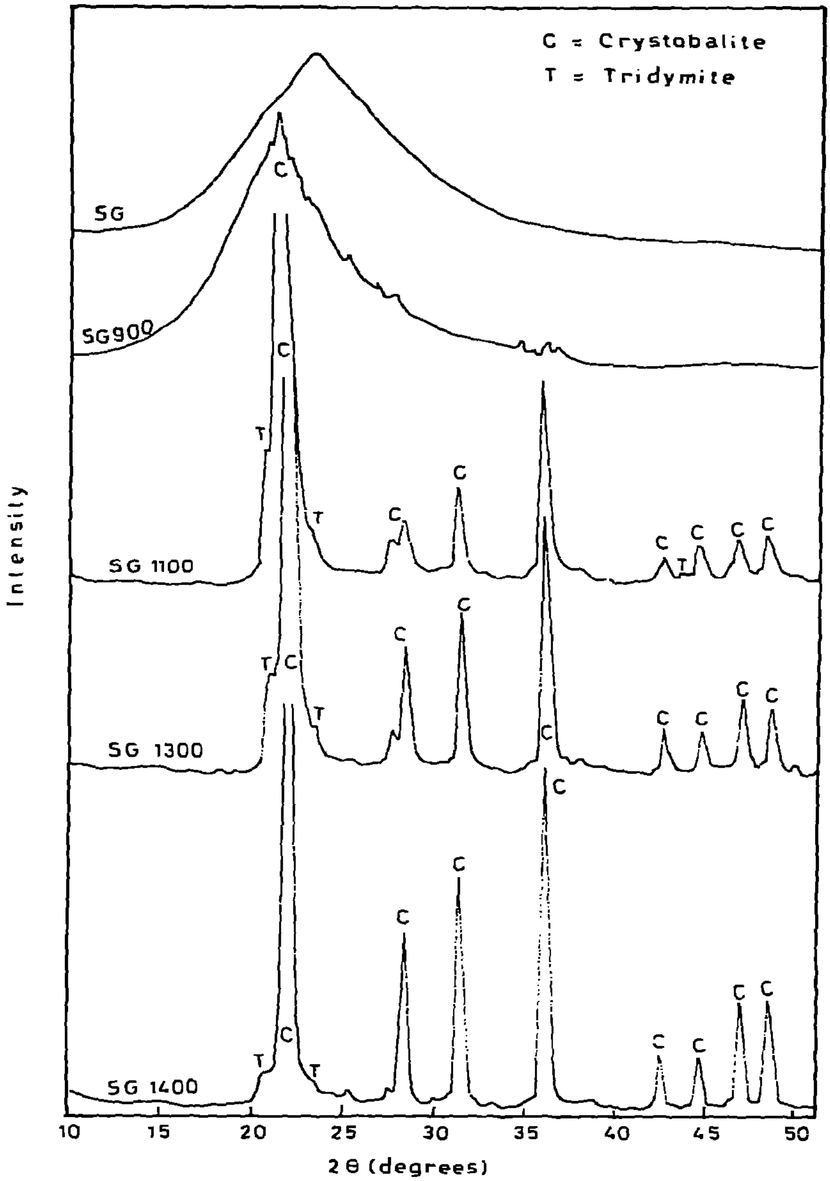

Fig. 4. X-Ray diffraction patterns of silica gel samples heated at various temperatures.

fraction patterns reveal the formation of poorly crystalline crystobalite at 900° C (see Fig. 4); the formation and subsequent crystallisation of this phase accounts for the slight decrease in surface area and total pore volume of the samples heated at 900° C and 1000° C. The formation of a crystobalite phase at 900° C is also associated with a marked increase in the particle size of the crystallites as calculated from X-ray analysis (Fig. 5). Heating at 1100° C is accompanied by the formation of a tridymite phase, as indicated by the X-ray diffraction pattern (Fig. 4); the formation of this unstable phase accounts for the increase in surface area and pore volume for the sample heated at 1100° C (Fig. 3). The subsequent crystallisation and consequent

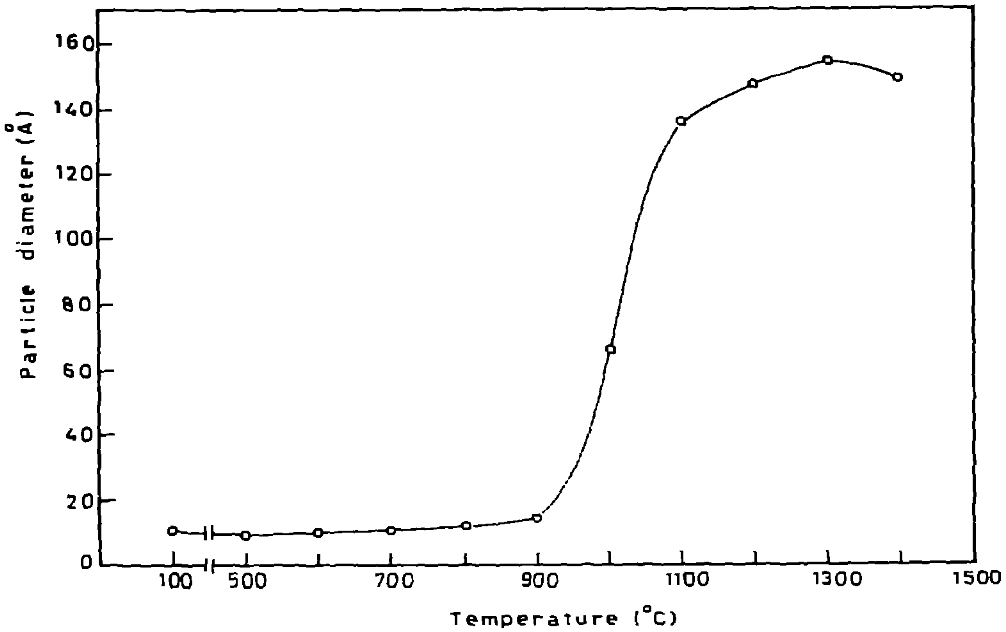

Fig. 5. Variation of the particle diameter of silica gel with temperature of thermal treatment.

increase in particle size of the crystallites account for the decrease in surface area and pore volume of the sample heated at 1300°C. However, the increase in the surface area and pore volume of the sample heated at 1400°C is mainly due to the decrease in particle size of the crystallites, as shown by X-ray diffraction (Fig. 5); the hydraulic radius of the total pore system is about 9 Å for the samples treated at 1300°C and 1400°C (Fig. 3).

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