

139. *The Production of Active Solids by Thermal Decomposition.*
Part X. Heat Treatment of the Xerogels of Silica.*

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Ion-free silica gel was prepared by the hydrolysis of silicon ethoxide, and separate portions were calcined at a series of fixed temperatures from 200° to 1460° c. Sorption isotherms of nitrogen, carbon tetrachloride, and methanol were then measured on the cooled product, its density was determined by immersion in three liquids (including mercury), and it was examined by *X*-ray and electron diffraction and by electron microscopy.

The average pore size remains almost constant from 200° to 900°, though both the specific surface and the pore volume (and with it the lump volume) diminish markedly; the loss of surface and of pore volume begins to accelerate in the region of the Tammann temperature (about 790° c). The sintering behaviour of silica, which is in marked contrast to that of, *e.g.*, ferric oxide, is due to the amorphous nature of silica, which persisted to *ca.* 1400°.

THE curve of specific surface against temperature of calcination of hydrous oxides is likely to show a continuous decline as temperature increases, if no new phase is produced when the water is driven off.¹ Silica gel is an oxide of a different kind from those previously considered, for (except after high-temperature treatment) it is amorphous, *i.e.*, it possesses only short-range order. Correspondingly the effect of heat on both surface area and pore structure shows interesting differences from that encountered with crystalline solids.

EXPERIMENTAL

Materials.—Ion-free silica gel was prepared by hydrolysis of silicon ethoxide by a method similar to that of Weiser, Milligan, and Coppac.² The ester in alcohol was poured, with stirring, into an excess of distilled water. Stirring was continued for 4 days, then the mixture was kept at room temperature for 3 months, after which a copious white gel had separated. This was filtered off at the pump and thoroughly washed with absolute alcohol by decantation to remove undecomposed ester. After filtration the solid was stirred with 2 l. of distilled water, and left for two weeks. Finally, the gel was spread out, air-dried at 25°, and broken into lumps.

On thermogravimetric analysis with the temperature of the furnace rising at 200° per hour, the product lost weight rapidly up to a furnace temperature of *ca.* 200°, then more slowly to much higher temperatures. There was no evidence for a stoichiometric hydrate and the results are consistent with the loss of water from a hydrous oxide.

Procedure.—Portions of the gels were heated for 5 hr. at a fixed temperature in the range 200—1460° on the thermal balance, and the properties of portions of the cooled product were examined as follows: (i) the specific surface by sorption of nitrogen at -183° volumetrically;^{1b} (ii) the sorption isotherm at 22° of the vapour of carbon tetrachloride and of methanol, with the electromagnetic sorption balance;³ (iii) the apparent density by immersion in mercury,⁴ carbon tetrachloride, or water⁵ (ρ_{Hg} , ρ_{CCl_4} , $\rho_{\text{H}_2\text{O}}$); (iv) (for selected samples) the *X*-ray powder photograph, the selected area diffraction pattern, and the electron micrograph; the electron optical examination was carried out with a Siemens Elmiskope I operated at 80 kv; portions of the solid were crushed and suspended in alcohol, a drop of this suspension being dried on a grid covered with a carbon film.

The water content *w* corresponding to each temperature of calcination was obtained by

* Part IX, *J.*, 1956, 3612.

¹ (a) Gregg, *J.*, 1953, 3940; (b) Gregg and Stevens, *J.*, 1953, 3951.

² Weiser, Milligan, and Coppac, *J. Phys. Chem.*, 1939, **43**, 1109.

³ Gregg, *J.*, 1955, 1438.

⁴ Goodman and Gregg, *J.*, 1956, 3612.

⁵ Cf. Culbertson and Dunbar, *J. Amer. Chem. Soc.*, 1937, **59**, 306.

repeating the calcination with a separate portion of the starting material, and then raising the temperature to 1000° until constant weight was obtained as registered on the thermal balance.

In addition, a portion of the starting material of each batch was examined dilatometrically: the solid was made into a paste with water, and then compacted by compression in a die (0.375 in. diam.) at 2000 lb./sq. in. by a hydraulic press. The compact, about 3 cm. long, was subjected, in a simple extensometer⁶ to a temperature rising steadily at 200° per hour, its length being read frequently.

The results for the isotherms (ii) and density (iii) led to separate estimates of the pore volume, V_I and V_D respectively. V_I could be calculated as x_s/ρ , where ρ is the density of the sorbate in the liquid form, merely by applying the Gurvitch relationship to the amount, x_s (g.), sorbed at saturation. The calculation of V_D depends on the fact that, with a pressure difference of 1 atm. across the meniscus, mercury cannot enter pores of diameter less than about 5 μ whereas the molecules of carbon tetrachloride and of water can penetrate pores with a diameter as small as *ca.* 5 Å or *ca.* 3 Å respectively. Thus the reciprocal of the density measured in mercury is the lump volume, and the differences $(1/\rho_{\text{Hg}} - 1/\rho_{\text{H}_2\text{O}})$ and $(1/\rho_{\text{Hg}} - 1/\rho_{\text{CCl}_4})$ are the volumes of pores with diameters between 5 μ and *ca.* 3 or 5 Å respectively. The calculations for both V_D and V_I are based on the assumption that the liquid or adsorbate retains its ordinary liquid density throughout the system; but if, as is probable, the density in the finest pores is higher than normal, the calculated pore volumes would be high (by perhaps a few %), and the enhancement might vary from liquid to liquid. This compression effect, combined with the further penetration of water because of its smaller molecular size, is sufficient to account for the small but not negligible difference between the pore volume measured by a given method with two different liquids (cf. Table). By combination of the values of pore volume with the

Temp.*	Colour	w †	θ ‡	ρ_{CCl_4} (g. cm. ⁻³)	$\rho_{\text{H}_2\text{O}}$ (g. cm. ⁻³)	$10^8 V/S'$ (cm.)
25°	White	13.5	1.0	—	—	—
200	"	6.5	0.46	2.06	2.18	6
400	"	4.0	0.32	2.09	2.21	5.8
600	"	1.75	0.16	2.11	2.27	6.1
800	"	0.55	0.07	2.16	2.27	6.4
900	"	0.2	0.04	2.13	2.27	7.4
1000	"	0.0	0.0	2.04	2.08	137
1100	Pale brown	—	—	2.12	2.07	231
1200	"	—	—	2.09	2.07	2200
1300	Brown	—	—	—	2.05	—
1400	"	—	—	2.05	—	—
1460	Grey	—	—	2.31	—	—

* Temperature of calcination (5 hr.).

† Volatile matter content (g. per 100 g. of SiO₂).

‡ Fraction of surface covered with chemisorbed water (assuming 1 molecule of H₂O occupies 15 Å²).

results of the measurement of specific surface (S') information as to pore structure is obtained. The simple volume : surface ratio V_D/S' or V_I/S' is useful; for a system of cylindrical pores of fairly uniform size V/S' is indeed equal to one half of the average pore radius, and for pores of more complicated shape, *e.g.*, the interstices between spherical particles of solids, the ratio still gives a useful approximation to an average pore width.

DISCUSSION

Results.—A striking feature is that the specific surface S' and the pore volume V both fall at approximately the same rate over a wide range of temperature: V/S' (and the average pore width) remains constant (within a few %) from 200—900°, even though both S' and V have fallen to less than one-half (Table; Fig. 1). The lump volume falls correspondingly as does the volume of the compact in the extensometer experiments (Fig. 1). These results are similar to those found by van Nordstrand, Kreger, and Ries⁷ with silica

⁶ Goodman, Thesis, London University, 1955.

⁷ van Nordstrand, Kreger, and Ries, *J. Phys. Chem.*, 1951, **55**, 621.

aerogel and a silica-bead catalyst. Now at the low temperatures considered, where actual migration of units of molecular or ionic size through the solid is improbable, the loss of surface must result from the adhesion of neighbouring primary particles, amounting to the removal of a pore. And if V/S' is to remain constant, such removal must occur without upsetting the rest of the lump. The remainder of the primary particles in the lump must retain their relative positions, so that the lost pore volume is in effect transferred to the outside of the lump, as shown by the fall in lump volume. The sorption isotherms of methanol and of carbon tetrachloride (Figs. 2 and 3) support the conclusion that the pore-size distribution does not change significantly as the temperature of calcination rises: they are of the same shape throughout, and the pressure at which the hysteresis loop opens changes remarkably little with temperature for a given adsorbate.

It is noteworthy that the sample at 200° (the lowest temperature for which there are data) has a pore volume not far different from the volume of the solid material (*ca.* 0.40 cm.³ g.⁻¹ as compared with 0.49 cm.³ g.⁻¹, carbon tetrachloride data being used). Thus the holes are of about the same size, shape, and number as the solid primary particles. The simplest model for this is of lumps of material made up of roughly cubic primary particles (of side *ca.* 50 Å), the holes corresponding to missing cubes. The loss of pore volume and surface up to 900° would then consist largely in local shifts of primary particles into neighbouring vacancies, which could occur without greatly upsetting the remainder of the lump if the bridges between particles were flexible. The model is, of course, oversimplified. The opacity of the gel shows that there are large pores having dimensions about the wavelength of light; the isotherms show that there is a *distribution* of pore sizes, for a single size would correspond to a vertical branch in the isotherm, *i.e.*, to a single pressure. Although it is unlikely that the particles are accurate cubes, the related model of equal spheres is less probable, for when a vacancy was filled by movement of a neighbouring sphere, there would be negligible loss of surface, since the moved sphere would touch its neighbours at isolated points only; more likely is some intermediate model, such as severely flattened irregular spheres.

The electron micrographs broadly support these inferences. (*a*) and (*b*) of the Plate show typical gel fragments from samples heated at 200° and 600°. They appear very similar, and at higher magnifications particles of the correct order of magnitude can be seen within the fragments. At higher temperatures, fragments showing smooth fracture edges become progressively more predominant. In (*c*) and (*d*) the small primary particles are no longer distinguishable although holes which may be portions of sealed pores are visible. However, in other fragments from the same samples [*cf.* (*e*) of Plate] particles of about 50 Å are discernible, providing good evidence that the loss of pore structure from some portions of the gel does not greatly influence the rest of the lump.

An essential feature of our model is the flexibility of the bridges; these could well be hydrogen bonds between hydroxyl groups of contiguous particles. Such bonds would be weak and not strongly directed, and the joining of neighbouring particles on sintering would involve the conversion of hydrogen bonds into siloxane bonds which are directional owing to their having partial covalent character, with consequent loss of flexibility. Thus the loss of pore volume and of surface should be accompanied by loss of "water," and accordingly it is satisfactory that the water content and the calculated fraction, θ , of surface covered by hydroxyl groups progressively diminish from 200° to 900° (see Table). The electron-diffraction patterns of samples heated below *ca.* 1460° have diffuse rings characteristic of liquids and amorphous solids (*e.g.*, glasses), showing that the solid possesses only short-range order, and implying that the structural units (silica tetrahedra) are joined randomly. When siloxane bridges form between contiguous amorphous particles, the composite particles must still be amorphous, for the original disorder remains. Moreover, the composite particle will tend to contain minute pores representing vestiges of the original, larger, gaps between the primary particles [(*c*) and (*d*), Plate].

Above *ca.* 700° the rate of loss of both pore volume and specific surface with rising

PLATE. *Electron micrographs (a to f) and electron diffraction pattern (g) of silica gel heated for five hours. The temperature of heating and the magnification are noted.*



(a)



(b)



(c)



(d)



(e)



(f)



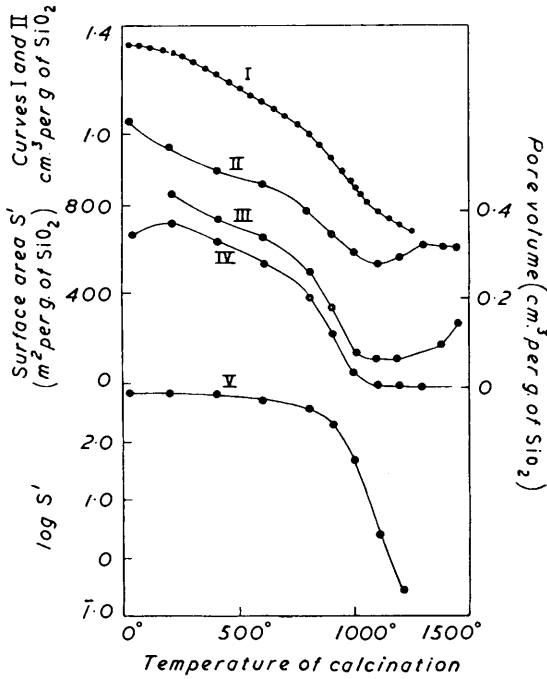
(g)

(a) 200° (× 51,000)
 (b) 600° (× 68,000)
 (c) 1000° (× 87,000)
 (d) 1100° (× 106,000)

(e) 1000° (× 200,000)
 (f) 1460° (× 206,000)
 (g) 1460°. Electron diffraction pattern of sample shown in (f)

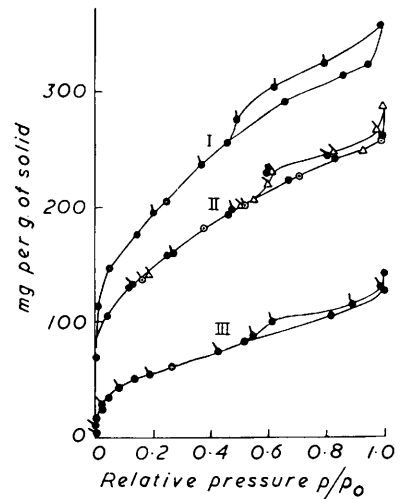
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FIG. 1. Calcination of precipitated silica.



I, Contraction; II, lump volume; III, pore volume; IV, surface area S' ; V, $\log S'$.
For curve I the sample was compacted at 2000 lb./sq. in. and was raised in temperature at 200° per hr. For curves II—V the sample was heated at the given temperature for 5 hr.

FIG. 2. Sorption isotherms of methanol at 22° on silica gel heated at I, 200°; II, 600°; III, 900° for 5 hr.



● 1st run, ○ 2nd run, △ 3rd run. Symbols with a "tail" denote desorption.

FIG. 3. Sorption isotherms of carbon tetrachloride. Conditions and symbols as in Fig. 2.

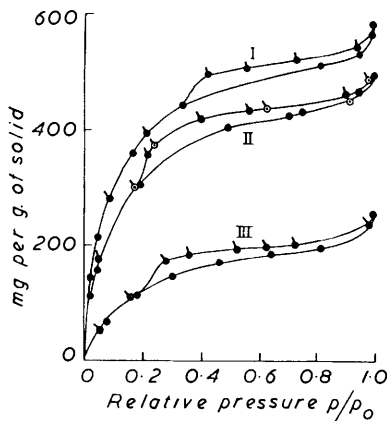
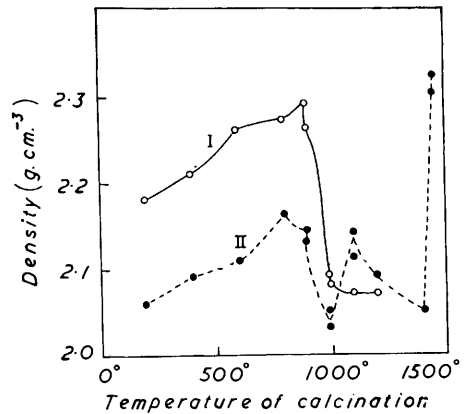


FIG. 4. Density of precipitated silica after calcination for 5 hr., determined by I, water; II, carbon tetrachloride.



temperature rapidly increases (Fig. 1). Milligan and Rachford⁸ found that the pore volume (measured by the uptake of water at saturation) of a commercial silica gel began to fall rapidly at 790° and by 900° was less than one tenth of its value at 600°. van Nordstrand, Kreger, and Ries⁷ found similar behaviour with a silica xerogel. Below *ca.* 1460° the gel is amorphous like a glass, and the temperature at which sintering accelerates can probably be identified with the well-known transformation temperature⁷ between the supercooled liquid and glassy states. At room temperature the viscosity (η) of glass is *ca.* 10^{20} poises so that viscous flow is almost undetectable, and the material behaves as an elastic brittle solid. At the transformation temperature the viscosity of silica is *ca.* 10^{13} poises. Since the coefficient of rigidity (n) of most solids is of the order of 10^{11} c.g.s. units, this implies that the Maxwell relaxation time (the relaxation time of stresses at constant strain, = η/n) is of the order of 100 sec. On a simple picture, then, it appears that the time of experiments has reached the time of atomic adjustments, and, consequently, the structural units have enhanced mobility. It seems likely that the enhanced sintering observed above 700° is caused by the increased mobility of the $(\text{SiO}_4)^{4-}$ tetrahedra when the Maxwell relaxation time becomes considerably less than the heating time of 5 hr.

Although the rate of sintering changes at *ca.* 700°, V/S' remains constant, showing that the qualitative effect of sintering remains unchanged. It seems likely that both above and below this temperature the sintering mechanism is the same and occurs by a viscous flow process; but below 700° the very high viscosity allows sintering to occur only in regions where adhesion is promoted by the conversion of hydrogen bonds into directed siloxane bonds.

Such behaviour may be contrasted to that of ferric oxide^{4,10} whose specific surface is largely reduced even at low temperatures. This solid being crystalline, the adhesion and growth of junctions can occur by movement of dislocations even at low temperatures, since the crystal lattice itself is the transport medium. It is noteworthy that the accelerated loss in pore volume occurs at approximately the Tammann temperature [half the m. p. ($^{\circ}\text{K}$)] for both silica and ferric oxide gels. With ferric oxide, however, this effect is believed to result from large-scale diffusion of ions (cf. Finch and Sinha¹¹), whereas with silica it is caused by the enhanced mobility of the $(\text{SiO}_4)^{4-}$ tetrahedra due to a reduction in viscosity.

Further data indicate that in the Tammann range the viscosity is not reduced sufficiently for crystals to grow. Thus the mobility of the $(\text{SiO}_4)^{4-}$ units must be considerably restricted, at any rate up to 1400°, for both the X-ray and the electron-diffraction results fail to show any marked ordering below this temperature. The anomalous results for density (Fig. 4) point in the same direction: the *fall* in density within the Tammann temperature range is most readily explained in terms of a sealing off, but not complete annihilation, of pores, a process which would result from a restricted mobility. A faint crystalite pattern was discerned in the X-ray powder photograph for 1400°, and the electron-diffraction patterns of the 1460° sample were highly crystalline. Individual crystals showing growth steps were isolable [(f), Plate] and the electron-diffraction pattern from this crystal (g) indicated twinning and stacking faults. We find an exactly analogous situation with glasses, where the transformation temperature lies considerably below the devitrification temperature.⁹ The sharp rise in density between 1400° and 1460° corresponds with the final elimination of pores and conversion of the solid phase into crystalline crystalite, but the intermediate rise between 1000° and 1100° determined in carbon tetrachloride is puzzling and may not be real; the considerable difference between the value measured in water and in carbon tetrachloride might denote the presence of pores

⁸ Milligan and Rachford, *J. Phys. Chem.*, 1947, **51**, 333.

⁹ See Jones, "Glass," London, Methuen and Co., Ltd., 1956.

¹⁰ Gregg and Hill, *J.*, 1953, 3945.

¹¹ Finch and Sinha, *Proc. Roy. Soc.*, 1957, *A*, **239**, 145.

capable of admitting only the latter and/or it could be caused by a relatively greater increase in density of water than of carbon tetrachloride at the surface of the solid. Probably both effects are present together.

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