830. *The Thermal Dehydration of Silica Xerogel Promoted by Alkaline-earth Chlorides.*

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The rate of dehydration of silica xerogel has been studied at a series of fixed temperatures from 300° to 970° in air. In addition, the effect on the dehydration rate of adding calcium, barium, and strontium chloride in concentrations up to 6·6 moles % has been examined. *X*-Ray and chemical analysis have been used to determine the extent of halide–gel interactions in the solid phase. Dehydration of silica gel surfaces is accelerated by these additives, probably by a catalytic effect below 800°, but above 800° formation of metal silicate occurs along with evolution of hydrogen chloride.

THE effect of heat treatment on the dehydration of the silica gel has been examined in studies of sintering.[1] Other investigations [2-4] have been made relating nitrogen and water-vapour adsorption by gels with the temperature of dehydration. The nature and pattern of the surface changes on dehydration appear to depend on the initial method of preparation [2,4] as well as on the time of heat-treatment and atmosphere.[5]

There are, however, no available data on the possible catalytic effect of impurities on the rate of dehydration and it was felt that such such a study could be made with a substantially hydrated oxide system, such as silica gel, by an examination of the weight losses at different temperatures. Alkaline-earth chlorides were chosen as the impurity for addition since these are often used [6] as mineralisers in synthetic silicate chemistry.

EXPERIMENTAL

Materials and Procedure.—Silica xerogel of 99·8% purity (principle impurities, iron and sodium) was kindly supplied by Mr. R. Worthington, Messrs. J. Crosfields and Sons Ltd. This had a surface area of 925 m.²/g. and a pore volume 0·55 c.c./g. (B.E.T.; N_2; 77°K). The gel was ground to pass a 300 mesh B.S. sieve, allowed to equilibrate at constant temperature and humidity for several days, and stored in a sealed container. This material when fired in air at 1000° or at 1450—1500°c for 6 hr. had a volatile matter content of 19·9% by weight. As might be expected, *X*-ray powder photographs showed an almost complete conversion into α-cristobalite after firing at the higher temperature.

The hydrated chlorides were all " AnalaR " materials, $CaCl_2,6H_2O$, $BaCl_2,2H_2O$, and $SrCl_2,6H_2O$. These were added as weighed portions to the gel and mixed by hand-stirring with a glass rod in a silica crucible for 45 min. (It was considered that this technique, when combined with further dispersion of the hydrate on melting, would give a nearly homogeneous distribution.) The weights taken were based on the amount of anhydrous halides present after slow heating at 240°. Since all these halides lose water of crystallisation at or below 200°, mole percentage additions were then calculated on a SiO_2 content of the equilibrated xerogel assumed to be 80·1% by weight.

The rate of dehydration in air was examined on a T.R. model Stanton thermobalance equipped with a nichrome furnace; a chart speed of 6″/hr. was used. In preliminary investigations to determine the possibility of decomposition or distillation of the separate halides up to 970°, no weight change except loss of water of crystallisation was detected (constancy of balance loading after small buoyancy corrections).

Several runs were also made in which the silica gel–mineraliser charge was varied from 1 to 5 g. and the experimental results were converted to a 1 g. basis. The results showed no dependence on sample weight. In subsequent experiments 4—5 g. charges were mostly used,

[1] Goodman and Gregg, *J.*, 1959, 694.
[2] Malanchuk and Stuart, *Ind. Eng. Chem.*, 1958, **8**, 1207.
[3] Milligan and Rachford, *J. Phys. Chem.*, 1947, **51**, 333.
[4] van Nordstrand, Kreger, and Reis, *J. Phys. Chem.*, 1951, **55**, 621.
[5] Kiselev, Leontzev, Lukjanovich, and Nikitin, *Zhur. fiz. Khim.*, 1956, **30**, 2149.
[6] Barrer, *Faraday Soc. Discuss.*, 1949, **5**, 326.

with repeat runs often with 1 g. quantities, all in silica crucibles. The weight trace could be read to ± 0.05 mg. and the temperature to $0.5°$.

Dehydrations were studied isothermally. The materials were first heated at 2°c/min. from room temperature to 260° and then held there until all water of crystallisation and physically adsorbed water had been driven off and a steady weight was recorded. The temperature was then allowed to rise at 20°/min. to certain values, generally 100° apart, and the furnace temperature controlled to give a constant value at this point. The weight loss was then recorded until a " steady value " was reached. The " steady value " was defined in all cases when the weight loss registered less than 0.5 mg. in 10 min. In general this required no more than 3 hr.

RESULTS AND DISCUSSION

Silica Xerogel.—Fig. 1 illustrates the pattern of weight losses at a series of constant temperatures for pure samples of xerogel. The results are plotted as the percentage of the total weight loss retained by the gel against time. By mathematical analysis it can be shown that the rate of loss of water at a given instant is, over the range of weight loss 5% to 95%, proportional to the content of water at that instant.
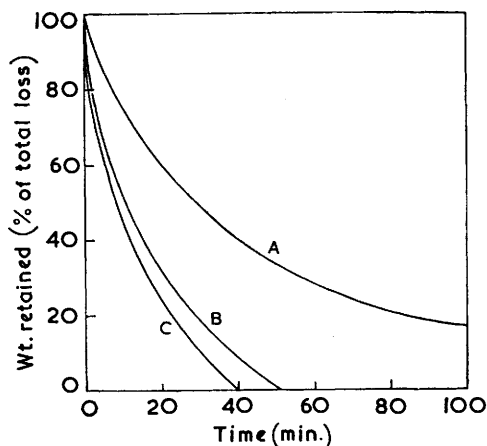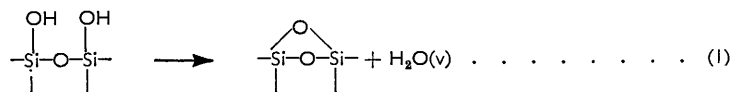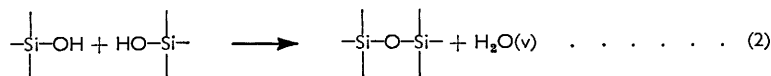

FIG. 1.   Isothermal pattern of weight losses.
A, 290°.   B, 500°.   C, 600°.

Dehydration probably involves elimination of water molecules by interaction of adjacent silanol groups on the external and pore surface of the gel. Thus, as proposed initially by Kiselev,[7]

$$\begin{array}{c} \text{OH} \quad \text{OH} \\ | \qquad | \\ -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- \end{array} \longrightarrow \begin{array}{c} \overset{O}{\overset{\diagup\diagdown}{}} \\ -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O(v) \end{array} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

or for reactions between adjacent particles and across micropores, we have:

$$-\overset{|}{\underset{|}{Si}}-OH + HO-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}- + H_2O(v) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

It is not possible to separate exactly the contributions of these two reactions at any temperature, although it is likely that reaction (1) predominates below 500—600° where viscous flow is not appreciable. Reaction (2) may also proceed at the narrow necks of bulbous capillaries, which will be present in the non-dehydrated material and will be formed further during calcination.

[7] Kiselev, " The Structure and Properties of Porous Materials," ed. Everett and Stone, Butterworths Scientific Publns., London, 1958, p. 195.

Effect of Alkaline-earth Chlorides.—(i) $BaCl_2,2H_2O$. This salt loses water of crystallisation at 962°. 0·7, 1·7, 3·2, 4·1, and 5·1 moles % was added in various experiments.

The average rates of dehydration [= total weight loss (mg.)/reaction time (min.) taken to the " steady value "] are given in Fig. 2 for three temperatures over the range of additions. The rate increases to a constant value at 1·7 moles % which is not affected further by increasing the barium chloride concentration to 5·1 moles %.

In conjunction with the dehydration experiments, separate samples of silica gel containing 5 moles % of barium chloride were calcined for 4 hr. above and below the m. p. of the chloride (at 800° and 970°, respectively). The samples were allowed to cool and subjected to chemical and X-ray analysis.
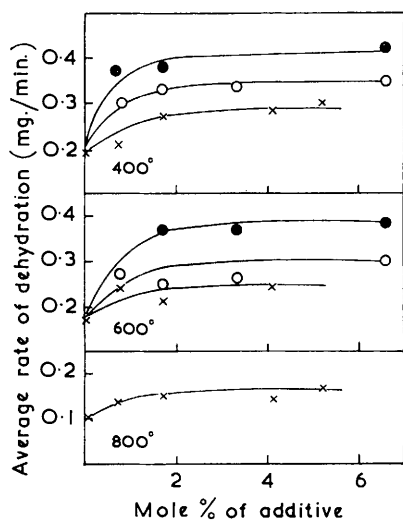

FIG. 2. Effect of alkaline-earth halides on dehydration rates.

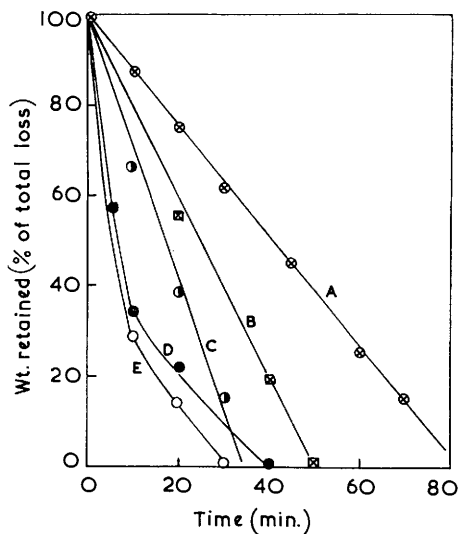× $BaCl_2$; ○ $SrCl_2$; ● $CaCl_2$.

FIG. 3. Effect of additives on weight losses at higher temperatures.

(A) 6·6 Moles % and (B) 3·4 moles % of $CaCl_2$ at 800°. (C) 1·7 Moles % and (E) 0·7 mole % of $SrCl_2$ at 800°. (D) 0·7 Mole % of $SrCl_2$ at 920°.

In the chemical analysis samples were immersed in water, boiled for 30 sec., and left overnight. The gel was then filtered off and washed and barium in the filtrate was determined gravimetrically as sulphate. For the samples calcined at 800° the barium recoveries were >99·9%, but for those calcined at 970° only 61·5—61·8%.

X-Ray analysis with Co-K_α radiation in an 11·46 cm. camera showed little crystalline matter in the product cooled from 800°. The pattern present was attributed to barium chloride, probably in the cubic form (A.S.T.M. 1-0948) with one additional line which might have been due to $BaSi_2O_5$. At 970° barium chloride was still present but there was excellent evidence for the formation of silicate, probably $BaSi_2O_5$ (A.S.T.M. 6-0316).

Qualitative experiments were also conducted in which the atmosphere above the melt was tested for effluent gas. At 800° no trace of gas could be detected; at 970° hydrogen chloride was identified.

(ii) $SrCl_2,6H_2O$ and $CaCl_2,6H_2O$. Dehydration was carried out with 0·7, 1·7, 3·3, and 6·6 moles % of strontium and calcium chloride, as above. It seemed necessary to see if the same effects were exhibited with these halides. Since the m. p.s are $CaCl_2$ 772° and $SrCl_2$ 873°, it would be more convenient with the present furnace to study the behaviour of the mixed systems in the vicinity of the halide m. p.

Fig. 2 includes the effects of these halides on the average dehydration rates at 400° and 600°. The results of increasing concentration are similar to that of barium chloride. The trend of weight losses with time at 800° and 900° depended on the halide concentration (Fig. 3). The same weight-loss pattern as for the xerogel (Fig. 1) was given by the 0·7 mole % mixtures, but marked differences were shown at the higher concentrations where the weight-loss curves became linear with time. (Steady values of dehydration rates were not determined for the 3·4 and 6·6 moles % additions of strontium chloride: these reactions were still proceeding after losses of 0·3—0·4 mg./min. for 90 min.)

The *X*-ray and analytical evidence given above, together with the results of Fig. 3, are interpreted as indicating the intervention of a solid–solid or solid–liquid reaction between components of the melt at and above 800°. With barium chloride, for example, the reaction probably proceeds by interaction of cleaved halogen ions with hydrogen of the silanol group, eliminating hydrogen chloride. This could occur within pores and between particles, giving sheet structures of $BaSi_2O_5$ as found in the clay minerals, with the barium atoms linking xerogel particles or pore walls. The initiation temperature is probably related to the nature of the xerogel. It is, approximately, the Tammann temperature of bulk silica $(0·5T_m)$, where the xerogel may be considered sufficiently " fluid " to enter into a solid reaction.

Below 800° the additives have a catalytic effect on the rate of dehydration while the extent of this is cation-sensitive. The largest cation (Ba^{2+}) gave the smallest increase in rate of dehydration. This may be explained by considering that the smaller the cation of the halide molecule the more readily will the molecule reach accessible sites of adjacent silanol groups, simply by having the most favourable migration and size factors.

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