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The Effect of Impurities upon the Physical Properties of Silica Gel by the Heat-Treatment

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The effects of various kinds of inorganic salts upon the physical properties of silica gel heated in the range up to 1200°C were studied. We measured the polymorphic behavior by means of X-ray diffraction, the simultaneous measurement of the differential thermal analysis, and the thermogravimetric analysis, and the specific surface area by means of the BET N_2 method and by means of studying the water-adsorption capacity. The cationic impurities which were found to have strong effects upon the physical properties mentioned above are Na^+, K^+, Ca^{2+}, Pb^{2+}, Cd^{2+}, Zn^{2+}, and Sb^{3+}. Cations such as Al^{3+}, Cr^{3+}, Mn^{3+}, and Co^{2+} were shown to have weak but positive effects upon the physical properties of silica gel.

The physical properties, such as the specific surface area and the water-adsorption capacity, of silica gel are known to be changed by heating at high temperatures. For instance, the specific surface area of silica gel is decreased by heating, as has been shown by Bastik,[1] and crystal growth was observed by Hirata[2] upon heating the precipitated silica. These changes seem partly due to the presence of impurities in silica gel. Also, Imelik and others[3] have studied the effects of sodium, potassium, calcium, and several other metal hydroxides upon the specific surface area, the pore volume, the mean pore radius, and crystallization by the high-temperature treatment of silica gel. However, the role of impurities was not made clear enough in these experiments. Moreover, quite a number of investigations of silica gel seem to have more or less ignored the effects of impurities when this material was subjected to high temperatures. Therefore, the influence of impurities upon the properties of silica gel heated at elevated temperatures was studied and will be described in this report.

Experimental

The material used in this study was Japan Industrial Standard Type-A and Fuji-Davison Co. Type-RD silica gel; it was purified by repeated washing with dilute hydrochloric acid and distilled water. The physical and chemical properties of the samples before and after purification are shown in Table 1, where the methods of measurements of these values are the same as those previously described.[4]

TABLE 1. SOME OF PHISICAL AND CHEMICAL PROPERTIES OF SILICA GEL USED IN THIS REPORT

Type of silica gel	Surface area (m^2/g)	Water adsorption capacity (wt %)		Na_2O (wt %)
		20% RH	90% RH	
RD as received	720	12.2	38.2	0.03
RD purified	720	12.2	38.2	0.007
A as received	650	11.0	35	0.2
A purified	650	11.0	35	0.01

The experimental procedures of impregnating various impurities and of pH adjustment are as follows; silica gel was suspended in aqueous solutions of various inorganic salts at given pH values at 50°C for 24 hr; then, after the mother liquid had been thoroughly removed from silica gel, it was used for further heat treatment at temperatures ranging from 200°C to 1200°C in air for 24 hr. The degree of the crystallization of amorphous silica as a function of the temperature was estimated from the ratio of the intensities of the X-ray diffraction lines of the (111) plane of β-cristobalite, the (101) and (100) planes of α-quartz, and the (101) planes of β-tridymite relative to that of the (211) plane of the precipitated calcium carbonate used as an inner standard (by mixing the latter material of 10% by weight with the samples). Flame spectroscopy was used for the determination of the Na^+, K^+, and Ca^{2+} ions, while photometric chelate titration was used for the deter-

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1) J. Bastik, *Bull. Soc. Chim. France*, **20**, 437 (1953).

2) Y. Hirata, *J. Japan Rubber Assoc.*, **31**, 920 (1958).

3) D. H. Everett Ed., "The Structure and Properties of Porous Materials," Butterworths, London, (1958), p. 266.

4) S. Kondo and M. Muroya, This Bulletin, **42**, 1165 (1969).

mination of the other metal cations. All data per unit weight of silica were obtained by heating silica gel at 1100°C.

Results and Discussion

(1) Polymorphism. In order to see the effect of the pH upon the thermal behavior of silica gel, X-ray diffraction patterns were taken on powder samples which had been adjusted to pH values of 3, 6, and 9 with acids and bases, such as hydrochloric, sulfuric, phosphoric, and boric acids and ammonium and sodium hydroxide, and which had then been heated at 1000°C for 24 hr. Marked diffraction lines of β-cristobalite, α-quartz, and β-tridymite were observed on the sample adjusted to pH 9 with sodium hydroxide, the rest of these samples showed very weak diffraction lines, except for the one adjusted to pH 3 with hydrochloric acid, which showed no diffraction lines. Figure 1 shows the X-ray powder diffraction lines of the samples prepared by suspending silica gel in an aqueous solution of sodium hydroxide (1% by weight (870 ppm Na$^+$)) and by then heating it at 700° and 1000°C for 24 hr respectively. At temperatues as low as 700°C, the crystallization from the amorphous state to β-cristobalite was seen very clearly, and α-quartz and β-tridymite seem to have grown at 1000°C. Well-shaped crystals were observed under the electron microscope on these samples. It seems clear from the results mentioned above that only sodium hydroxide had a marked effect on crystallization, but had little effect on the pH adjustment. Since Na$^+$ and/or OH$^-$ ions seem to play a major role in crystallization, the effects of other sodium salts with various anions, such as F$^-$, Cl$^-$, Br$^-$ and SO$_4^{2-}$, of varied concentrations were examined under the same experimental conditions as above. The relative diffraction intensities of the (111) planes of β-cristobalite which appeared on these samples were dependent upon the concentration of the Na$^+$ cation, but not on the kind of anion, within the range of experimental error. Figure 2 shows the relation between the relative diffraction intensities of the (111) planes of β-crystobalite and the concentration of the Na$^+$ cation in the form of various sodium salts. As may be seen in this figure, crystal growth becomes remarkable in the presence of more than about 800 ppm of Na$^+$ cations, but is almost negligible in the presence of less than 100 ppm of Na$^+$ cations. The reason for the absence of diffraction lines on the sample adjusted to pH 3, mentioned previously, in that the sample was purified in that preparation.

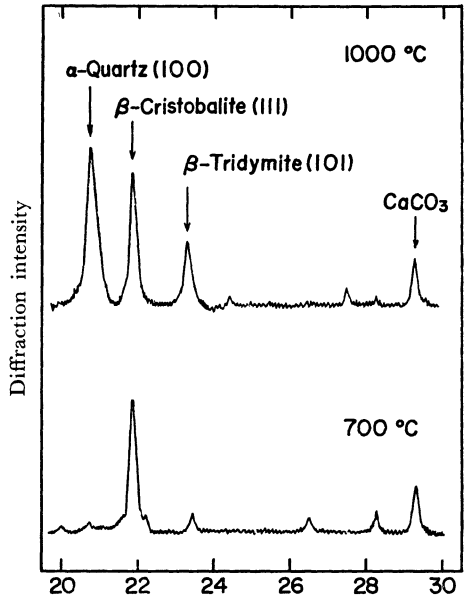

Fig. 1. X-Ray powder diffraction lines of silica gel containing 870 ppm Na$^+$ cation and heated at 700° and 1000°C for 24 hr.

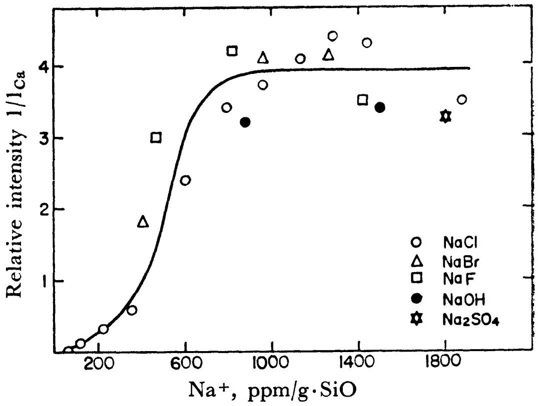

Fig. 2. The curve for plot of the relative intensity of X-ray diffraction lines of (111) planes of β-cristobalite grown by heating silica gel at 1000°C against the concentration of Na$^+$ cation contained in silica gel.

(2) Differential Thermal Analysis and Thermogravimetric Analysis. The DTA and TGA measurements were carried out on the sample containing 600 ppm of a Na$^+$ cation in the form of NaCl, as may be seen in Fig. 3, in order to ascertain the thermal behavior of silica gel accompanied by the phase transition from the amorphous to the crystalline phase or from one crystalline phase to another crystalline phase. The experimental conditions for DTA and TGA measurements were the same as have been described before.[5] As may be seen in this figure, four endothermic peaks accompanied by a weight decrease in TGA and two exthothermic peaks with no discontinuous change in TGA were observed. The mechanisms

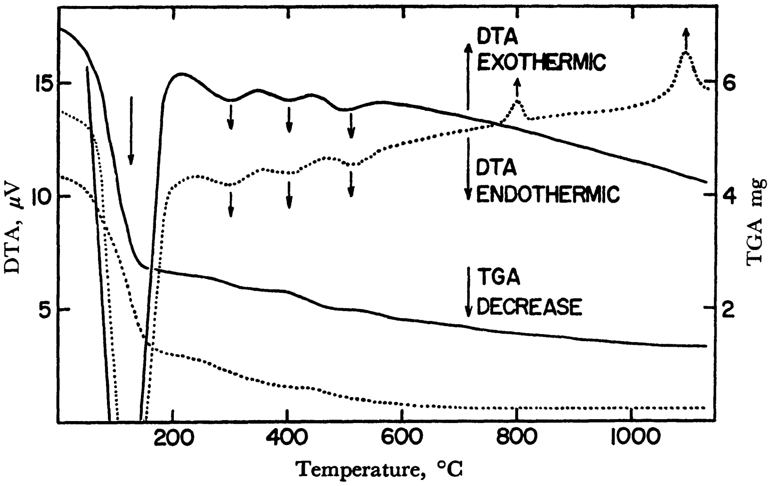

Fig. 3. DTA and TGA curves of silica gel. Full lines and dotted lines show those of silica gel containing 50 and 600 ppm Na+ cation respectively.

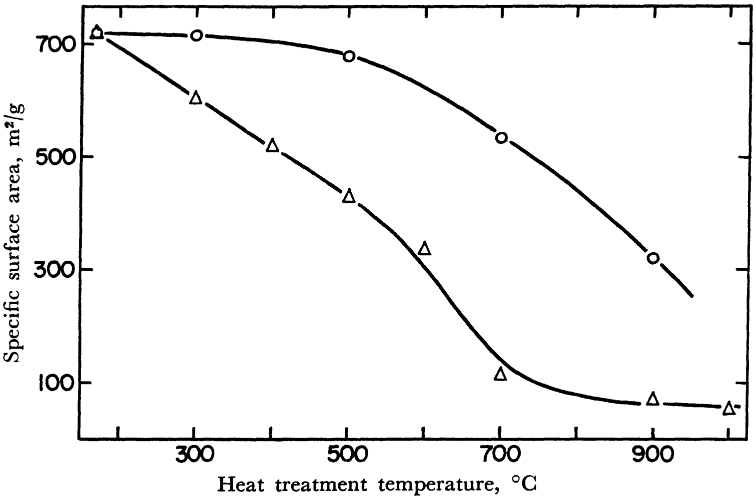

Fig. 4. Curves of the specific surface area *versus* heat-treatment temperature of RD type silica gel. Circles and triangles show results of the sample containing 50 and 600 ppm of Na+ cation respectively.

of these four endothermic reactions were discussed in a previous paper⁵⁾ from the point of view of the dehydration of surface silanol. Since the two exothermic reactions had no discontinuous weight change, the one at 800°C can be attributed to the phase change to β-cristobalite, and the other, at 1100°C, to the phase change to α-quartz and/or β-tridymite; this is supported by the results of the X-ray diffraction experiments described above. On the other hand, no exothermic peak was observed in this temperature range on the sample containing 50 ppm of the Na^+ cation. Since it is now clear that the Na^+ cation has a major effect upon the crystal growth of silica gel, the effects of the salts of other cations, such as chlorides, sulphates, and nitrates of cations such as K^+, Ca^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, Pb^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}, and Sb^{3+}, were tested by the procedures described above. The results of these experiments can be summerized as follows.

1) The influence on the growth of β-cristobalite was marked in the cases of cations such as Na^+, K^+, Pb^{2+}, and Sb^{3+}, and very weak but positive in the cases of cations such as Cr^{3+} and Al^{3+}; 2) the growth of α-quartz was influenced strongly by cations such as Ca^{2+}, Cd^{2+}, and Zn^{2+}, and less strongly by cations such as Mn^{2+}, and Co^{2+}, and 3) the rest of the cations tested had no observable effect upon the growth of either crystal. The combination of group 3) cations with those of group 1) or 2) did not also have an observable

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5) S. Kondo and M. Muroya, This Bulletin, **43**, 2657 (1970).

effect on the crystal growth.

(3) Specific Surface Area and Water-adsorption Capacity. In the above section it was shown that many of the cationic impurities had a strong influence on the crystal growth at higher temperatures; this was studied by means of X-ray diffraction. Therefore, it is interesting to see the effect of those ions not only at high temperatures, but also over a wider temperature range, upon other properties of silica gel, such as the specific surface area (SA) and the water-adsorption capacity. The SA values of the RD-type samples containing 50 and 600 ppm of the Na^+ cation as a function of the temperature of heating for 24 hr are shown in Fig. 4. The SA of the sample containing 600 ppm of the Na^+ cation shows a big decrease in the range from 200°C to 700°C, and becomes almost constant at higher temperatures. On the other hand, that of a relatively pure sample remains almost constant up to 500°C and starts to decrease gradually at higher temperatures. Figure 5 shows the influence of the Na^+ cation concentration upon the SA of RD-type samples heated at 700°C for 24 hr. In this figure, the effect of the Na^+ cation becomes bigger at concentrations of approximately more than 100 ppm. These results indicate the remarkable effect of some of the impurity ions on the decrease of SA, even at relatively low temperatures.

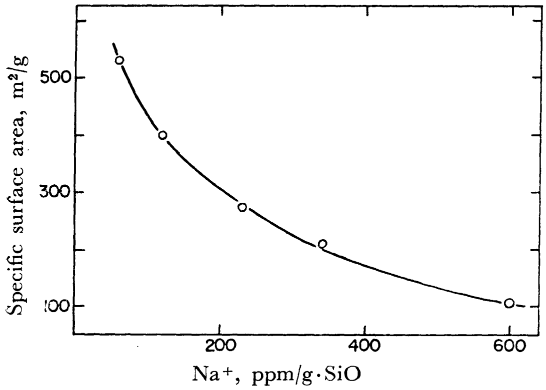

Fig. 5. The relation between the specific surface area and the concentration of Na^+ cation contained in RD type silica gel heated at 700°C for 24 hr.

Figure 6 shows the curves of the plot of the water-adsorption capacities at relative humidities (RH) of 20 and 90% at 23°C against the heat-treatment temperatures on the samples discussed in the above section. In Fig. 6, the values of the purer samples are much higher than those of the less pure samples. The general tendency of the curves of 20% RH is similar to that of the SA-temperature curves. Since the amount of water adsorbed at 20% RH corresponds approximately to an amount a little more than a monomolecular layer, it is reasonable to see a close similarity between the curve of 20% RH in Fig. 6 and that in Fig. 4. Because the adsorption capacity at 90% RH is usually compared with the pore volume, the big decrease in the value at 90% RH at higher temperatures of heat-treatment can be interpreted as a decrease in pore volume or as the effect of sintering.

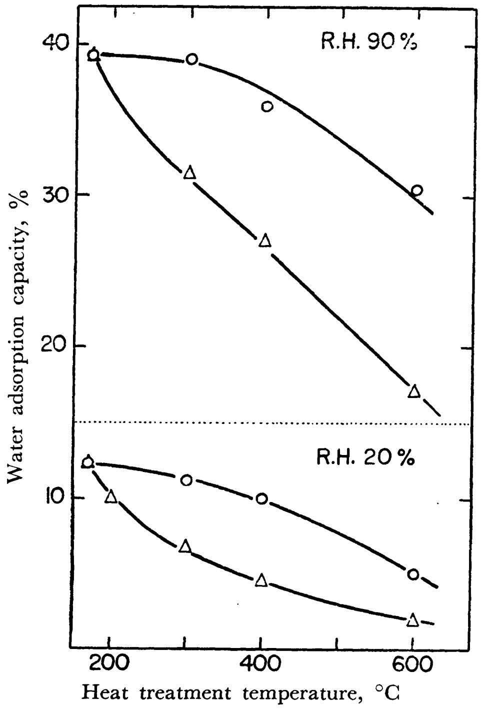

Fig. 6. Curves of the water adsorption capacity *versus* the temperature of heat-treatment. Circles and triangles show those of RD type samples containing 50 and 600 ppm Na^+ cation respectively.

Summary

Such physical properties as the polymorphic behavior, the thermal properties, the specific surface area, and the water-adsorption capacity of silica gel are largely changed when it is heated in the presence of cationic impurities such as Na^+, K^+, Pb^{2+}, Ca^{2+}, Cd^{2+}, Zn^{2+}, and Sb^{3+}. Weak effect upon the physical properties mentioned above were observed in the cases of such cationic impurities as Al^{3+}, Cr^{3+}, Mn^{3+}, and Co^{2+}.

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