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The Surface Structure of Silica Gel Studied by Dielectric Dispersion[*1]

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The effect of water adsorption and heat treatment at various temperatures between 200 and 1100°C on the dielectric dispersions of silica gel was measured in the frequency range from 50 to 3×10^6 Hz and 9.81 GHz and in the temperature range from -196°C to 180°C. Two anomalous dispersions (Dispersion I and II) and one anomaly (Anomaly III) were found. The mechanisms of those anomalies were discussed in relation to some physical properties and silica crystal structures. Dispersion I, having activation energy ΔE equal to 11 to 14 kcal/mol, can be ascribed to the monomolecular layer of adsorbed water. Dispersion II, with activation energy of about 5 to 7 kcal/mol, can be attributed to proton diffusion through hydrogen-bond chain of surface silanol groups. Anomaly III, having activation energy of about 3 kcal/mol, may be assigned to dipolar rotation of free silanol.

Recent studies of the surface structure of silica gel by means of dielectric measurements,[1-3] infrared spectroscopy[4] and so forth have revealed many interesting aspects in detail. However, there are still some ambiguities on the nature of surface silanols and their interaction with adsorbed molecule. In this report, dielectric dispersions of silica gel were studied in respect to the effect of heat treatment and water adsorption and some interpretations of these results in combination with other physical properties are given in view of the surface structure of silica gel.

Experiment

Dielectric Measurement. The dielectric constant of silica gel in the frequency range from 50 to 3×10^6 Hz was measured with an Ando Electric Model TR-1 transformer-bridge. A dielectric cell A in Fig. 1 is composed of two coaxial cylindrical electrodes in a glass container with electric capacity of about 10 pF. The temperature of the cell can be changed from -196 to 180°C with the constancy of less than ±1°. The dielectric constant at 9.81 GHz was measured by a transmission-line method. In this case, the sample holder was constructed so that the atmosphere and temperature of the holder could be controlled easily from -60 to 100°C within ±1°.

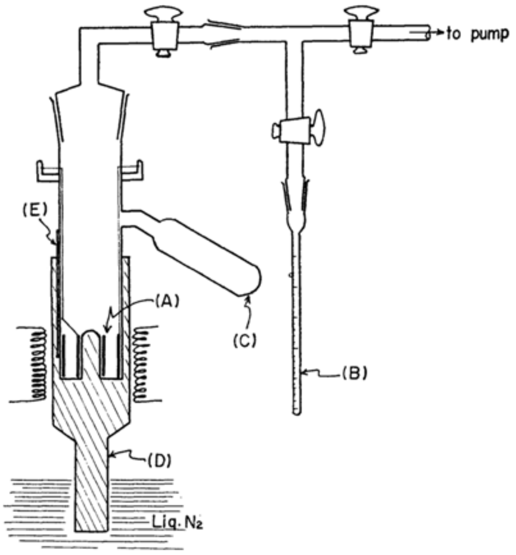


Fig. 1. Low frequency dielectric cell (A), with water burette (B), borosilicate or quartz glass tube for heat treatment (C), copper block (D), and Cu-Constantan thermocouple (E).

In order to obtain the real part of the dielectric constant ε', from the apparent value E, measured with powder sample, Pearce's equation[5] was used.

[*1] Presented at the spring meeting of Japan Applied Physics Society, 1967.

1) J. Le Bot and S. Le Montagner, *Compt. Rend.*, **233**, 862 (1951).

2) K. Kamiyoshi, *Sci. Rep. Res. Inst, Tohoku Univ.*, **5**, 93 (1957).

3) K. Kamiyoshi and J. Ripoche, *ibid.*, **8**, 239 (1960).

4) J. B. Peri, *J. Phys. Chem.*, **70**, 2937 (1966); L. R. Snyder and J. W. Ward, *ibid.*, **70**, 3491 (1966).

5) C. A. R. Pearce, *Brit. J. Appl. Phys.*, **6**, 358 (1955).

$$\frac{E-1}{\varepsilon'-1}=\frac{(1-v)P}{1-vP} \qquad (1)$$

Here, v is the parameter which is determined empirically and P is the volume filling factor, being equal to the ratio of bulk density of packed powder and particle density listed in Table 1. Values of the dielectric constant of powder materials of known dielectric constant obtained by this method are in good agreement with those of literature in the range under investigation.

TABLE 1. CHEMICAL COMPOSITION AND PHYSICAL PROPERTY OF SILICA GEL

Na_2O	0.01%
Fe	0.005%
Al	0.03%
Specific surface area	700 m^2/g
Pore volume (V_p)	0.35 cc/g
Particle density (d)	1.24 g/cc

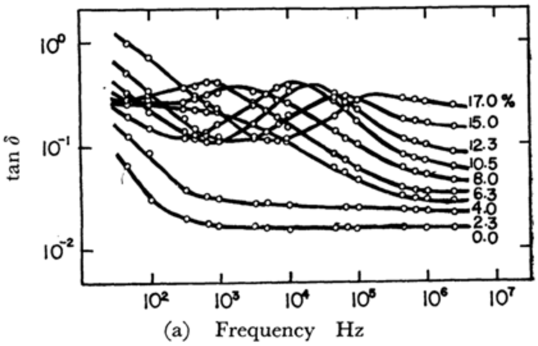
Material. Silica gel was synthesized from sodium silicate and sulferic acid of analytical grade and washed carefully with dilute hydrochloric acid and distilled water. The material dried was powdered to less than 80 mesh. Some of the physical and chemical properties of the sampe thus obtained are shown in Table 1, where specific surface area, S m^2/g, was determined by BET method using nitrogen and pore volume, V_p cc/g, by liquid immersion method using ethyl alcohol. Particle density, d g/cc, of silica gel granule, which is the aggregate of primary particles having the density of 2.2 g/cc, was calculated by the following formula.

$$d=\frac{1}{V_p+1/2.2} \qquad (2)$$

The amount of water adsorbed on silica gel was obtained by drying a known amount of sample in cell A in Fig. 1 at 170°C for two hours under vacuum of 10^{-4} mmHg and then introducing to cell A a necessary amount of water in burette B which was degassed beforehand. Silica gel was heat-treated in vacuum of 10^{-4} mmHg in the quartz container C at various temperatures from 200 to 1100°C for about 2 hr and then transferred to A. There is no exposure of silica gel to the atmospheric air in the procedure.

Experimental Results

Effect of Adsorbed Water (Dispersion I). Figure 2(a) shows the curves of tan δ *versus* frequency of silica gel at 23°C having various amount of adsorbed water. The heights of tan δ maxima of these curves are roughly proportional to water content of silica gel from 0 to 10% as seen in Fig. 3. Those heights become approximately constant beyond 10% water but the accompanying increase of tan δ background level makes the measurement less accurate. Since the monomolecular layer of water is completed statistically at about 10% water, this anomaly may be interpreted as related to this statistical monomolecular layer. Tan δ maxima change with temperature as seen in Fig. 2(b), in a similar manner to tan δ *versus* frequency curves in Fig. 2(a). In this figure, we find another one at lower temperature side being discussed in



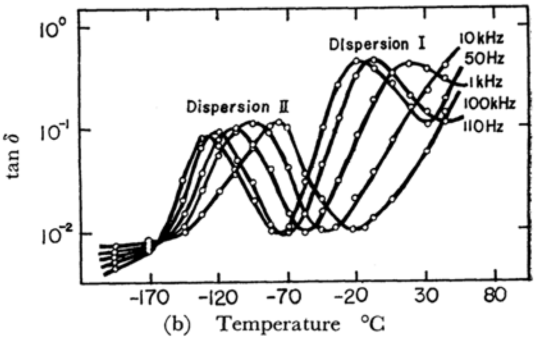


Fig. 2. Dielectric loss of silica gel with various water content.
(a) shows the frequency *versus* tan δ curves at 23°C.
(b) shows the temperature *versus* tan δ curves at 5.3% water adsorption.

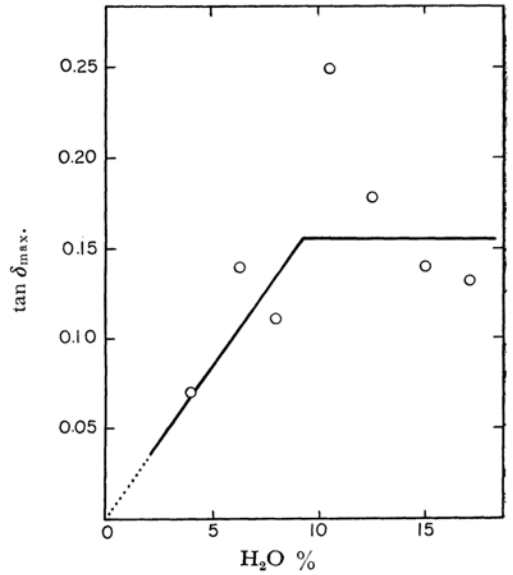


Fig. 3. Relation between the peak heights of tan δ maxima and water content of silica gel of Dispersion I at 23°C.

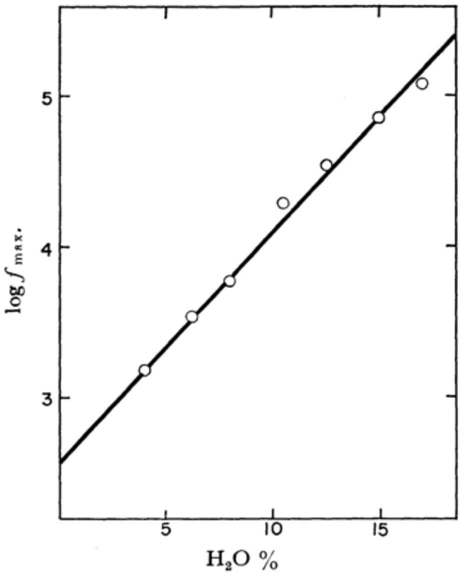


Fig. 4. Log frequency of tan δ maximum of Dispersion I *versus* water content of silica gel at 23°C.

the next section. In Fig. 4, water content is proportional to the shift of frequency of tan δ maximum at 23°C. At constant frequency, water content is proportional to the temperature of tan δ maximum.

Figure 5 shows the curves of complex dielectric constant *versus* frequency at 5.3% water adsorption and 23°C. These curves are characteristic of dielectric dispersion, so this anomaly will be called Dispersion I hereafter in this report. Cole-Cole arc plots of Dispersion I at 5.3% shown in Fig. 6 deviate largely from semi-circle law and indicate a large distribution of relaxation times. However, it is difficult to tell whether Dispersion I is the Debye or Maxwell-Wagner type from data available in this study. Figure 7 shows the curves of log relaxation time, τ, *versus* reciprocal temperature obtained from Cole-Cole arc plots, mentioned above, at various temperatures, together with the values at 11.5% water adsorption measured by Kamiyoshi.[2] Table 2 shows activation energies ΔE and constant τ_0 of Dispersion I and those by Kamiyoshi[2] and of ice measured by Auty and Cole.[6] These values of Dispersion I are close to those of ice and differ from that of water. This similarity suggests the existence of some kind of ordered configuration of

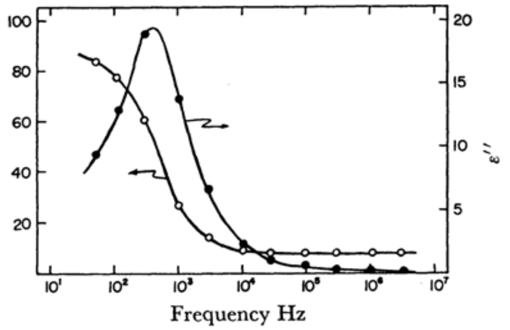


Fig. 5. Frequency *versus* complex dielectric constants, ε' and ε'', curves of Dispersion I of silica gel of 5.3% H_2O and at 23°C.

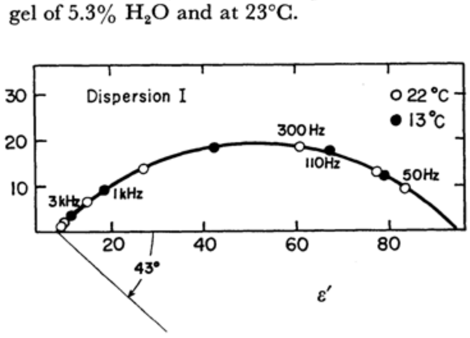


Fig. 6. Cole-Cole arc plots of Dispersion I of silica gel of 5.3% H_2O at 13 and 22°C.

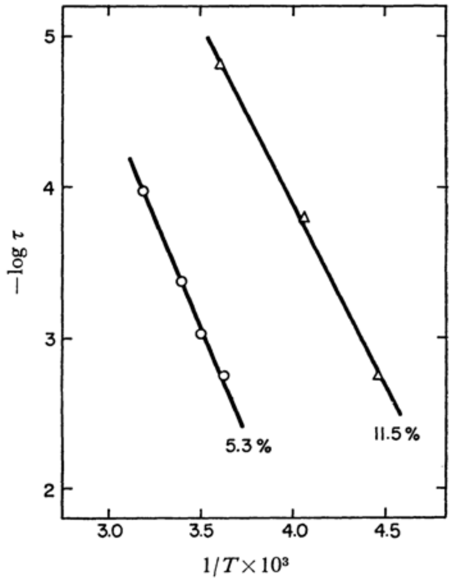


Fig. 7. Log relaxation times τ *versus* reciprocal temperature of Dispersion I by the present investigation and by Kamiyoshi[2] shown by circular and triangle plots respectively.

TABLE 2. ACTIVATION ENERGY ΔE AND RELAXATION TIME τ_0 OF DISPERSION I OF SILICA GEL CONTAINING ADSORBED WATER AND OF ICE[6]

H_2O %	ΔE (kcal/mol)	τ_0 (sec)
5.3	14.2	2.5×10^{-16}
11.5*	11.3	5.9×10^{-15}
ice	13.2	5.3×10^{-16}

* These were obtained by Kamiyoshi.[2]

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6) R. P. Auty and R. H. Cole, *J. Chem. Phys.*, **20**, 1309 (1952).

adsorbed water molecule on silica gel surface, which will be discussed in section IV.

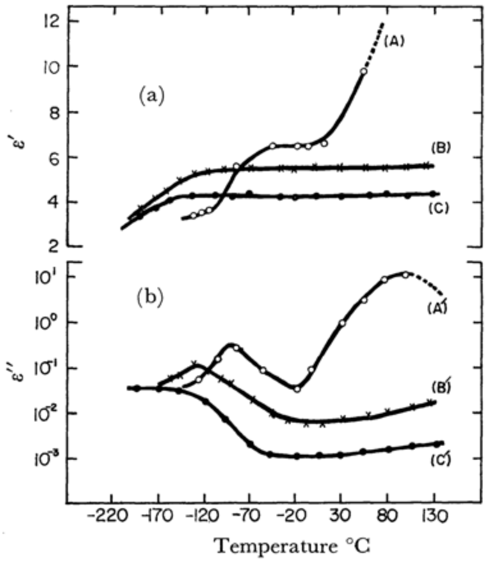

Fig. 8. Real and imaginary parts of complex dielectric constants *versus* temperature curves are shown in figures (a) and (b) respectively. Curves (A), (B) and (C) show those values at 1% H_2O, and 200 and 300°C of heat-treatment of silica gel, respectively. Note Dispersion I appearing at higher temperature.

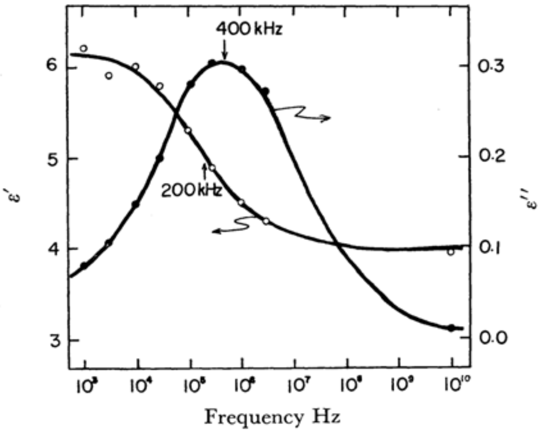

Fig. 9. Frequency *versus* complex dielectric constant curves of Dispersion II of silica gel at −58°C and 1% H_2O.

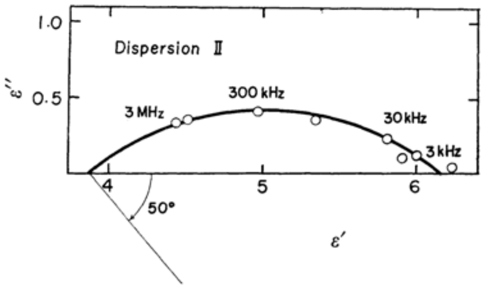

Fig. 10. Cole-Cole arc plots of Dispersion II of silica gel at −58°C and 1% H_2O.

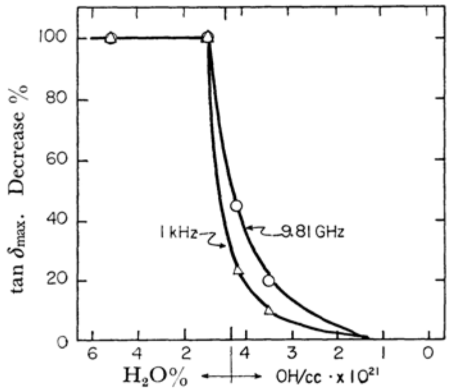

Fig. 11. Relation of decrease of the height of tan δ maxima shown by per cent of Dispersion II to water content and OH concentration per unit volume of silica gel.

Silica Gel Without Adsorbed Water (Dispersion II). Figure 8(a) and (b) show the curves of ε' and ε'' at 1 kHz against temperature of silica gel thermally treated at 200 and 300°C (curves B, C, B′ and C′) and those of 1% water adsorption (curves A and A′). The anomaly at 1% water adsorption of curves A and A′ is Dispersion I as described in section 1. The anomaly at −100°C can be observed not only in curves A and A′ but also in curves B, B′, C and C′ in which silica gels are treated at higher temperature. The curves of ε' and ε'' *versus* frequency of this anomaly at −58°C and 1% water adsorption for example, as seen in Fig. 9, suggest this anomaly to be a dielectric dispersion (Dispersion II). In this figure, the frequency of inflection point of ε' curve, about 200 kHz, differs from that of ε'' maximum, about 400 kHz, and this discrepancy suggests Dispersion II being the Maxwell-Wagner type. Cole-Cole arc plots of Dispersion II, shown in Fig. 10, indicate the existence of large distribution of relaxation times as often seen in colloid system.[7] Figure 11 shows the height of tanδ maxima of Dispersion II at 1 kHz and 9.81 GHz against water adsorption and the concentration of silanol groups per unit volume which is equal to the weight loss by heating in the form of water divided by particle density at the temperature of heat treatment. ε'' maxima are not affected by the amount of water adsorption, become smaller by the decrease of hydroxyl concentration (or the increase of temperature) and are unobservable at about 500°C. The

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[7] S. Oka, "Theory of Solid Dielectrics," Iwanami Press, Tokyo (1964), p. 161.

values of ε' decrease also by elevating temperature and become almost constant and equal to that of vitrous silica above 500°C. This shows the decrease of contribution of polar silanol groups to the dielectric constant. From those results, it seems reasonable to assume Dispersion II to be caused by the diffusion of ion such as proton through hydrogen-bond chain of surface silanol groups.

The relation of log frequency of ε'' maxima of this dispersion to the reciprocal temperature is shown in Fig. 12 on silica gel treated at four different conditions; 5.3 and 1% water adsorption and 200 and 300°C of heat treatment. ε'' maxima at 2.89 GHz obtained by Le Bot and Le Montagner1) and at low frequency by Kamiyoshi and Ripoche3) on silica gel both dried at 110°C (about 1% water adsorption) are well on the line of 1% water of the present investigation. Table 3 shows the activation energies obtained from Fig. 12. The activation energies at 5.3% and 1% water are much larger than those without water. This may suggest the higher potential barrier for ionic diffusion by the presence of bound water. It should be added that Dispersions I and II have been found with deuterium-exchanged silica gel showing similar behavior to the ordinary silica gel.8)

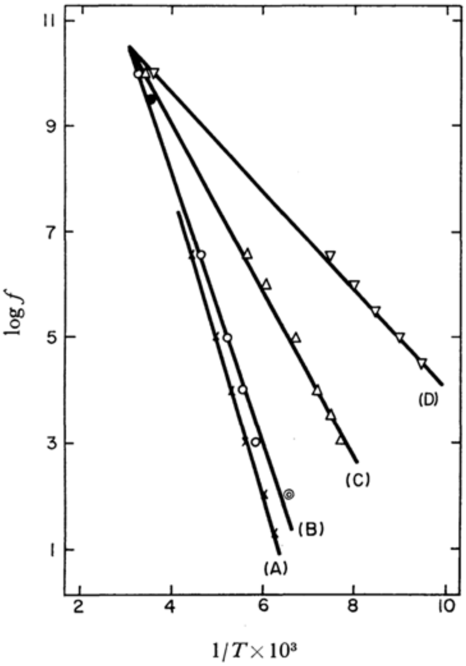

Fig. 12. Log frequency *versus* reciprocal temperature curves of Dispersion II of silica gel, in which (A), (B), (C) and (D) show those of 5.3% H_2O, 1% H_2O, and 200 and 300°C of heat treatment respectively and black and double circles show the values measured by Le Bot1) and Kamiyoshi2) respectively.

TABLE 3. ACTIVATION ENERGY ΔE AND RELAXATION TIME τ_0 OF DISPERSION II OF SILICA GEL CONTAINING ADSORBED WATER AND TREATED THERMALLY

	ΔE (kcal/mol)	τ_0 (sec)
5.3 H_2O %	14.0	4.0×10^{-21}
1.0 H_2O %	11.4	1.9×10^{-18}
200°C	6.8	8.3×10^{-16}
300°C	5.0	1.6×10^{-14}

High Temperature Heat Treatment (Anomaly III). A very small maximum of ε'' can be observed at −178°C and at 1 kHz on silica gel treated at 500°C as seen in Fig. 13. This maximum becomes smaller by elevating the temperature of heat treatment and becomes unobservable at 1000°C. Therefore, this anomaly may be related to silanol groups existing above 500°C. Owing to the smallness of this anomaly, it is difficult to obtain the values of dielectric constant accurately and sufficiently enough to tell whether this is a dielectric relaxation. However, an approximate activation energy was obtained from the dependency of ε'' maximum frequency on temperature. ΔE and τ_0 are equal to about 3 kcal/mol and 1×10^{-10} sec respectively. The smallness of the activation energy suggests that this anomaly might be caused by the rotation of free silanol dipoles surviving after heat treatment.

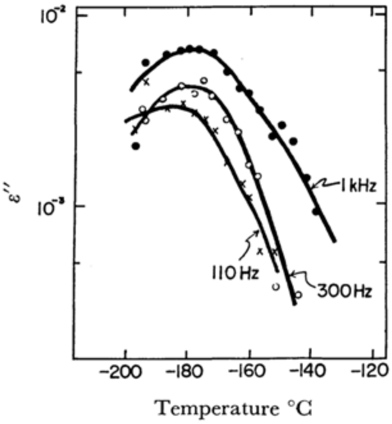

Fig. 13. Curves of imaginary part of the complex dielectric constant *versus* temperature of silica gel heat-treated at 500°C.

Discussion

The weight loss of silica gel by heating is usually considered to be caused by desorption of adsorbed water and condensational dehydration of surface

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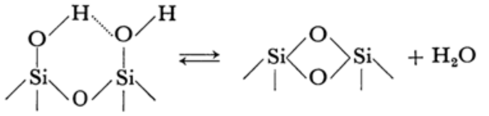
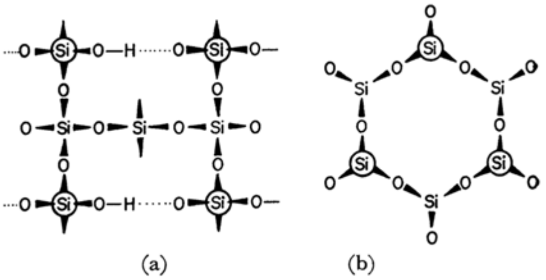
8) S. Kondo and M. Muroya, presented at the 21st Annual Meeting of The Chemical Society of Japan, 1968.

silanol groups. However, it is difficult to distinguish between each other by such means as thermogravimetric analysis and infrared spectroscopy. In the latter case, a broad and strong band at about 3500 cm^{-1} and at room temperature becomes gradually weaker by heating and almost disappears at about 600°C. On the other hand, a sharp band at 3750 cm^{-1} which is very obscure at low temperature becomes clear by heating. This latter band starts to decrease from about 600°C and disappears at 1000°C. The 3500 cm^{-1} band can be assigned to the hydrogen-bonded O–H stretching vibration of either adsorbed water or surface silanol. Since adsorbed water desorbs almost completely at 200°C as studied by the thermal behavior of Dispersion I, this band above 200°C may be assigned to the hydrogen-bonded silanol groups, in which the Dispersion II of this report originates.

Models to illustrate the structure of this type of hydrogen-bonded surface silanol have been proposed by several authors[4,9] as shown below.



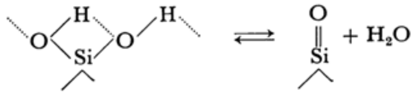
With such a model, however, it seems rather difficult to construct a reasonable siloxane skeletal structure in three dimensions and to satisfiy such physical properties of the surface as silanol surface density of about 8/100 Å^2. Moreover, the dehydration reaction according to this model requires a considerable distortion of valence angle of surface siloxane or deformation of succesive skeletal siloxane, which would cause changes of physical properties such as the decrease of surface area. This is not likely because the surface area decreases markedly only above about 500°C and drastic change of the structure starts above 700°C depending upon the nature of impurities.[10]



(a) (b)

Fig. 14. (a) and (b) are (100) and (111) crystal planes of cristobalite respectively. Rounded Si atoms are on the top surface.

In this report, the model as shown in Fig. 14 (a) and (b) is taken into consideration under the assumption that primary particle of silica gel has a very short range order of siloxane structure similar to some of the silica crystals such as cristobalite, tridymite and quartz. In these crystals the silicium atom exposed on the crystal plane surface can possess one or two hydroxyl groups depending upon the index of the plane. Figure 14 (a) and (b) show the (100) and (111) planes of cristobalite as example, since the density of silica gel, 2.2 g/cc, is almost equal to that of cristobalite and silica gel changes to cristobalite most easily by heating. In Fig. 14 (a), each silicium atom on the (100) plane can have two hydroxyl groups which would form hydrogen-bond chain with each other with the distance of about 2.7 Å and whose surface density is 7.85/100 Å^2. Dispersion II may be attributed to the proton diffusion through those one-dimensional chains of hydrogen-bond. Without adsorbed water, the activation energy for this diffusion may not be as large as that with the presence of adsorbed water as seen in Table 3. The dehydration reaction with this model would be as follows;



although we have no evidence for the existence of Si=O.

In such a model, the first layer, at least, of adsorbed water might have some kind of very short range order which may be three dimensional by including substrate structure, and the activation energy for the proton diffusion would be larger than that of water and close to that of ice as shown in Table 2. Considering the statistical nature of this quasi-crystalline model, the distribution of relaxation times may be large, as shown in this report.

The Anomaly III and the 3750 cm^{-1} band can both be assigned to free silanol groups. It might be interesting to see that silicium atoms on the (111) plane of cristobalite, as shown in Fig. 14 (b) for example, can have one hydroxyl group whose distance to each other is about 5 Å and is too far to form a hydrogen-bond and which has low surface silanol density of 4/100 Å^2. The dehydration reaction of such type of silanol requires some rearrangement of skeletal structure at high temperature and leads to the decrease of specific surface area and crystal growth.[10]

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9) R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell Univ. Press, Ithaca, New York (1955), p. 243.

10) F. Matsuyama, B. S. Thesis, Osaka Univ. of Education, 1968.