The Thermal Behavior of Silanol Groups of Silica Gel as Studied by Infrared Spectroscopy. I*

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(Received July 4, 1973)

The thermal behavior of the silanol of silica gel has been studied by quantitative infrared spectroscopy. Transparent and glass-like plates of silica gel of high purity, after they had been heat-treated at various temperatures below 680 °C, were used for the measurement of OH stretching vibrations ranging from 3100 to 3800 cm^{-1}. These absorption bands were analysed into the several component bands by the simulation method using a Dupont Co. Curve Resolver. The intensity of these bands in area were proportional to the OH concentrations as measured by the thermal method. Each component band disappeared at a temperature which was roughly equal to that obtained from the dielectric and conductivity measurements. From these results, assignment was attempted on the basis of these bands.

The nature of the silanol group of high-specific-surface-area silicas, such as silica gel, aerosil, and porous glass, has been studied in many laboratories in relation to its electric, thermodynamic, optical, and many other physical properties.[1,2] Among them, infrared spectroscopy has been proved to be one of the most useful tools for the investigation of the bond nature of the surfaces of these substances. In the case of aerosil, the broad absorption band of the silanol group has been extensively studied, and a few absorption bands have been reported to exist in this broad band. However, the analysis of these bands is not clear enough except for those very near to 3750 cm^{-1}. Also, few infrared absorption experiments have been carried out on silica gel because of the difficulty of preparing a specimen suitable for the infrared measurement. The purpose of this paper is to try to make a quantitative analysis of the absorption band of silica gel and to study some properties of the resolved component bands.

Experimental

Materials. Ethyl orthosilicate was hydrolyzed to silica sol in the presence of hydrochloric acid at about 70 °C and gelled on a plastic plate such as Teflon. The hydrogel thus formed was dried in air at room temperature. A thin glass-like plate, about 0.15 mm thick and 1 cm^2 wide, was obtained; the infrared transmittance of this sample at 4000 cm^{-1} was about 80%. The specific-surface-area, as determined by the BET N_2 method, and the weight loss of this sample when heat-treated at various temperatures are shown in Fig. 1. The pore volume was 0.33 cc/g. No alkali and alkali earth impurities were detected with the flame spectroscopic analysis within limits of experimental error of about ± 1 ppm in the case of the sodium ion in silica gel.

Infrared Spectroscopy. The spectrophotometers used in this work were Japan Spectroscopy Co. types IRA-2 and 402G, and Hitachi Works Co. type IR 225. The absorp-

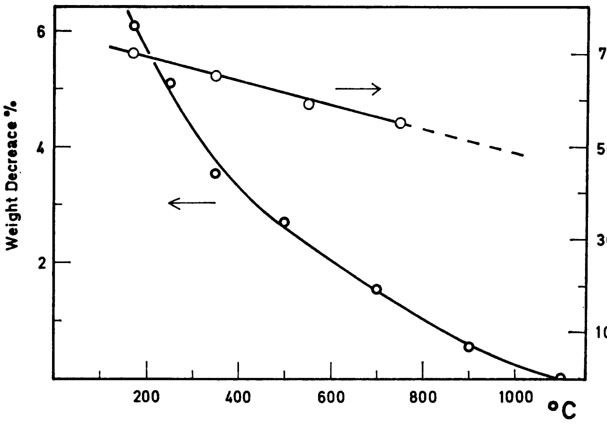

Fig. 1. The effect of heat-treatment on the weight decrease and the specific-surface-area of silica gel

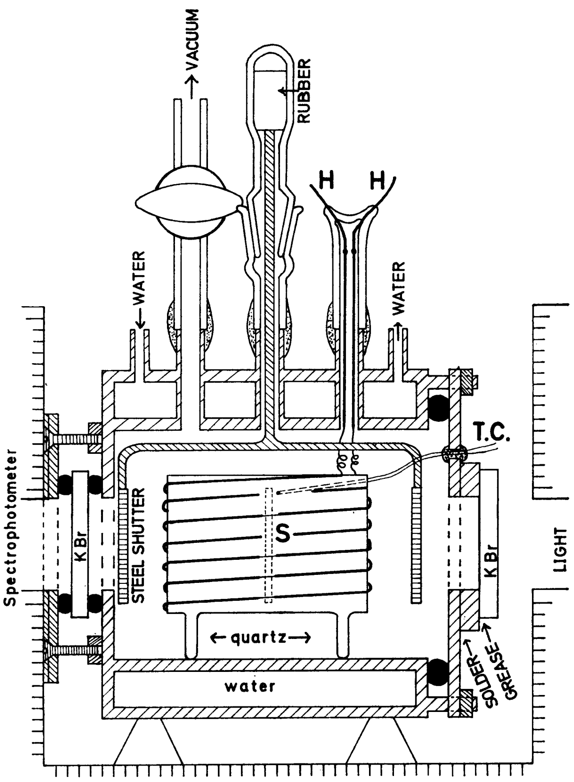

Fig. 2. High temperature vacuum cell for the infrared spectroscopy. The shaded, blank, black, and dotted areas show brass, glass, O ring and "Torr Seal" adhesive respectively unless otherwise specified.

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* presented at the 23th (1969) and 27th (1973) annual meetings of the chemical Society of Japan and the 23th (1970) Colloid and Surface Chem. Symposium.

tion cell used in this experiment is shown in Fig. 2. The specimen was kept fixed in a furnace capable of heating the sample up to about 680 °C under a vacuum of 1×10^{-3} Torr. The absorption band was taken at room temperature *in vacuo*. No contamination of silica gel by the oil used in producing the vacuum was seen as far as the infrared spectra were concerned. The absorption intensity was estimated with the accuracy of about ±4% by measuring the area of the absorption curve within the range of the transmittance from about 80 to 20%; in this range the transmittance is practically linear to the extinction coefficient.

The absorption bands thus obtained were resolved into their component bands with Lorentz, Gauss, and mixed types by means of a Dupont Co. Curve Resolver, type 310. It was fairly easy to find the most reasonable combination of component bands with this simulation method. More details of the infrared measurement will be shown elsewhere.[3] The experimental error of the temperature measurement of the specimen was about ±4%.

Results and Discussion

As is well known, the broad absorption band between 3800 and 3000 cm^{-1}, as is shown in Fig. 3(a), can be assigned generally to the OH bond of silanol groups and adsorbed water of silica gel at 70 °C. Upon repeated heavy water adsorption, this band shifts quickly and uniformly to the OD stretching region, keeping its original OH band shape quite well. By elevating the heat-treatment temperature, this broad band at 70 °C becomes narrower—for example, at 180 and 360 °C, as is shown in Figs. 3(b) and (c) respectively; at 680 °C in Fig. 3(d) the band shape is sharp as a result of the condensation and dehydration reaction of silanol. Heating was done sufficiently long to attain the equilibrium condition (constant absorption intensity), as is shown in the upper part of Fig. 5.

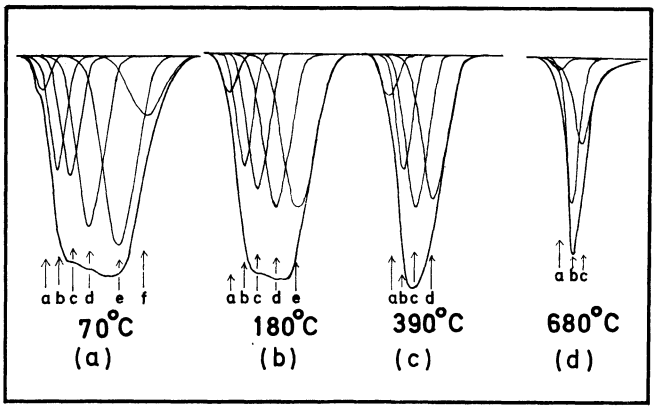

Fig. 3. OH stretching absorption bands and their component bands of silanol in various heat-treatment temperatures. *a*, *b*, *c*, *d*, *e*, and *f* show the maximum wave numbers of the component bands at 3870, 3750, 3630, 3470, 3260, and 3030 cm^{-1}, respctively.

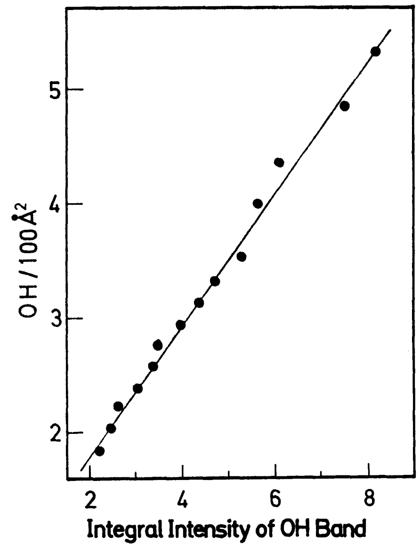

Fig. 4. The relation of the integral intensity of OH band in arbitrary scale to the concentration of silanol per 100 Å².

In Fig. 4 a good linear relationship can be seen between the intensity of these bands, being equal to the area of the absorption curve and the hydroxyl concentration of the sample at the corresponding temperature; this relationship can be obtained from Fig. 1 by dividing the weight decrease by the specific-surface-area. Therefore, the concentration of the silanol under given conditions can be estimated by using this curve derived from the infrared spectra.

The shape of the band at 680 °C is not symmetrical; it can be satisfactorily simulated as the sum of the three component bands at 3870, 3750, and 3630 cm^{-1}± 10 cm^{-1}, as is shown in Fig. 3(d). The 3750 and 3630 cm^{-1} bands agree with the literature,[1,2] while the 3870 cm^{-1} band seems to be newly found in silica gel in this work. The shapes of the 3750 and 3630 cm^{-1} bands were nearly Lorentzian, while that of the 3870 cm^{-1} band was almost Gaussian in type. The broader

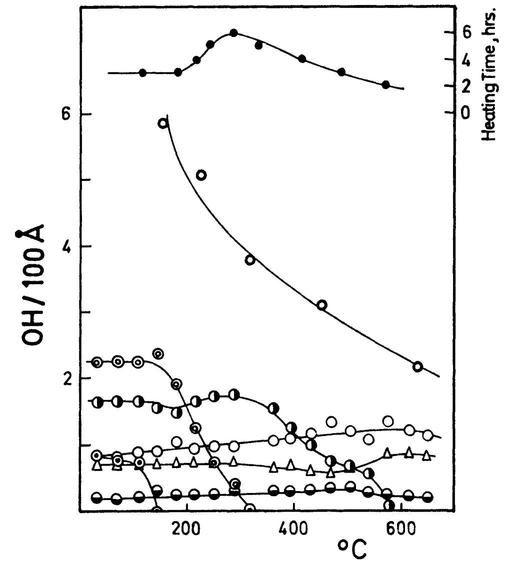

Fig. 5. The relation of the silanol concentration of the absorption bands and their component bands and the heating time to the heat-treatment temperature of silica gel.

O: Total OH, ⊙: 3030 cm^{-1}, ◎: 3260 cm^{-1}, ◑: 3470 cm^{-1}, ○: 3630 cm^{-1}, △: 3750 cm^{-1}, ◒: 3870 cm^{-1}.

bands at lower temperatures could easily be analyzed to their component bands in a similar manner; in order they were shown from the higher to the lower temperatures, in Figs. 3(c), (b), and (a). At 70 °C, the broad band was found to consist of six component bands, with their maxima at 3870, 3750, 3630, 3470, 3260, and 3030 $\text{cm}^{-1}\pm 10\ \text{cm}^{-1}$. The existence of the 3470, 3260, and 3030 cm^{-1} bands seems to have been made clear in this work. The concentration of silanol corresponding to each of these component bands can be obtained from the total concentration of silanol at a given temperature multiplied by the fraction of the area of each of these component bands in relation to the total area of the absorption band at this temperature. The results are plotted in Fig. 5. In this figure, the OH concentration of each component band decreases successively by elevating the heat-treatment temperature. The 3030 cm^{-1} band disappears at about 150 °C and can be assigned to adsorbed water, since this temperature agrees well with the temperature of the desorption of adsorbed water obtained from our TGA, dielectric, and conductivity measurements.[4-6] The intensity of the 3260 cm^{-1} band began to decrease at about 150 °C, the temperature of disappearance of the 3030 cm^{-1} band. The same is true for the 3470 cm^{-1} band as may be seen in this figure. These two bands disappear at about 330° and 580 °C respectively. These bands can be assigned to the hydrogen-bonded silanols with various bond energies. During the decrease in these bands, the maximum wave numbers of these bands shift slightly to higher wave numbers, as is shown in Fig. 6. This blue shift may be interpreted in the following two ways: 1) it may be the result of the weakening of the hydrogen-bond interaction of the neighboring atoms following the dehydration reaction; 2) more likely, each component band may be composed of a few secondary components and the dehydration reaction may proceed from the lower-wave-number part of these secondary components.

Since the decrease in the intensity of one band and the increase in that of the other type does not seem to have occurred simultaneously in Fig. 6, the possibility of such a generation of one type of silanol as a result of the condensation of another type or types of silanols is very small.

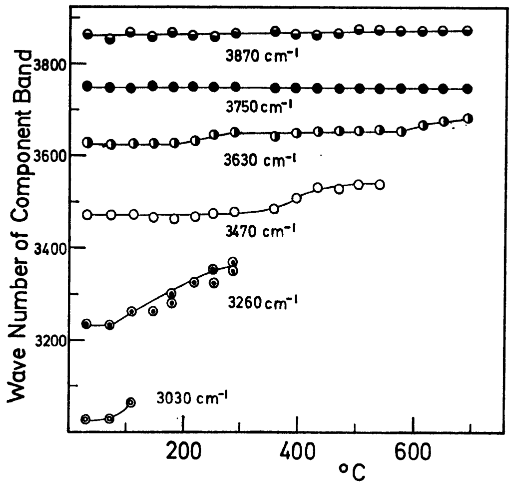

Fig. 6. The shift of the component bands by the elevation of the heat-treatment temperature.

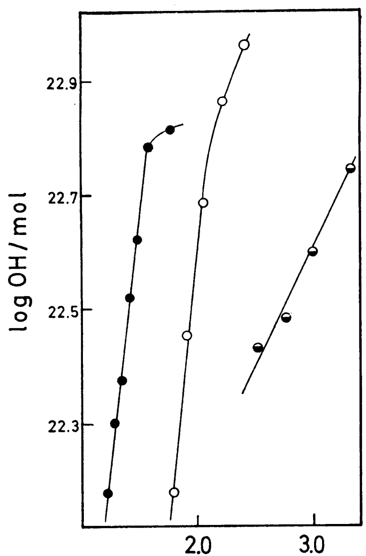

Fig. 7. The logarithm of the silanol concentration of component bands as a function of the reciprocal temperature of heat-treatment.
◒: 3030 cm^{-1}, ○: 3260 cm^{-1}, ●: 3470 cm^{-1}

Table 1.

OH band in cm^{-1} $\pm 10\ \text{cm}^{-1}$	Temperature of dissociation in °C $\pm 4\%$	ΔH kcal/mol ± 0.2 kcal/mol	O-H···O Distances in Å	Assignment
3030	150	1.9	—	Adsorbed water
3260	330	8.9	2.7	H-bond OH
3470	580	8.1	2.8	H-bond OH
3630	—	—	3.0	? H-bond OH
3750	—	—	—	Free OH
3870	—	—	—	?

The OH equilibrium concentrations of 3030, 3260, 3470, and 3630 cm^{-1} bands are proportional to the reciprocal temperatures in the temperature range of dehydration reaction, as may be seen in Fig. 7. From these relations, we can obtain the enthalpy values, ΔH, of the dehydration reaction of these silanols, as is shown in Table 1. These values are very small compared with that of the usual chemical reaction. Table 1 also shows the O—H···O bond distances estimated from the relation between the absorption frequencies and the O—H···O distances of various compounds,[7] and their possible assignments.

The intensities of the 3630, 3750, and 3870 cm^{-1} bands did not change in the temperature range measured in this study. The 3750 cm^{-1} band, which is assigned to the free silanol, can also be found in other types of silica. However, this band of silica gel overlapped with the 3870 and 3630 cm^{-1} bands pretty heavily even at 680 °C, in contrast with that of aerosil, which can be clearly seen without overlapping at 700 °C.[1] Therefore, it was not possible to resolve the 3750 cm^{-1} band into its components as in the case of aerosil.[8,9] The OH band at about 3630 cm^{-1} was also found in aerosil.[10-12] However, there are some differences in the deuterium exchange behavior and, hence, in the interpretations between these two materials.

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