The Characterization of the Hydroxyl Surface of Silica Gel

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The properties of silica gel were studied as a function of the hydrothermal treatment of hydrogel by means of the nitrogen-adsorption isotherm, the mechanical strength, thermodilatometry, and infrared spectroscopy. As a result, the number of contact points between primary particles of silica was found to decrease, and closed pores were found to be produced, by this treatment. The analysis of the infrared absorption spectra of the OH groups of this material showed that there are three kinds of OH groups in silica gel; (1) free OH groups on the outer surface of primary particles, which can adsorb molecules easily, (2) weakly perturbed OH groups inside closed pores, and (3) strongly hydrogen-bonded OH groups on the surface around the contact points. The relative concentration of these OH groups changes drastically upon the hydrothermal treatment; this is in accord with the change in the macroscopic properties mentioned above.

The properties, such as the specific surface area and the pore-size distribution of silica gel, are highly sensitive to its history, starting from the polymerization of monomeric silicic acid to the physical and chemical treatment before and during use.[1] Many of these characteristics are controlled by surface OH groups of this material. For instance, the infrared absorption band of the OH stretching vibration is changed in shape not only by heat treatment,[2,3] but also by different methods of synthesis. However, the reason for this change is not yet fully understood. Another example is the values of the surface OH densities of various colloidal silicas, which fluctuate widely from less than 4 $\mathrm{nm^{-2}}$ to even more than 10 $\mathrm{nm^{-2}}$ from one sample to another.[4] The purpose of this paper is to try to clarify the complex nature of the OH groups of silica gel and its relation to the surface and pore structures through the infrared spectroscopy of silica gel, which has been prepared by the hydrothermal treatment of hydrogel. Three different kinds of sites have been found for OH groups on the surface in various kinds of slica gel, as will be described below.

Experimental

Fractionally distilled silicon tetraethoxide was used as the raw material for synthesizing silica gel of a high purity. Silicon tetraethoxide (1 mol) was hydrolyzed at 70 °C for 95 to 105 min with 10 mol of distilled and deionized water, whose pH has been adjusted to 2.0 with hydrochloric acid. Silica sol thus obtained was rapidly cooled to about 0 °C and then poured into flat vessels with air-tight covers in order to make a thin liquid film of the desired thickness. This sol was kept still for 24 h at 17 °C, by which time it set to hydrogel. This hydrogel was washed with water to remove the hydrochloric acid and ethanol, and was then stored in water below 10 °C. This hydrogel was sealed in Pyrex glass ampoules with distilled and deionized water of pH 5.9 and was then heated in an autoclave at various temperatures. The hydrogel thus treated was dried slowly at 10 °C for 48 h. Finally thin plates of xerogel less than 0.05 mm thick and 1—2 $\mathrm{cm^2}$ wide were obtained. The influence of Pyrex glass seemed negligible, since the properties of this product were almost the same as those of substances made in ampoules of high-purity quartz glass under the same conditions.

The infrared spectra of these samples were taken after the desorption of adsorbed water at 180 °C *in vacuo* and *in situ* in a cell described elsewhere.[2]

Results and Discussion

The specific surface area and the total pore volume of this material change remarkably upon the hydrothermal reaction of hydrogel. Figure 1 shows nitrogen-adsorption isotherms of silica gel hydrothermally treated at various temperatures for 2 h. These curves indicate that this material changes from the micropore type to the macropore type with an increase in the temperature of treatment, as is well known. Figure 2 shows the curves of the specific surface area and the total pore volume against the reaction time during hydrothermal treatment at 100 °C. The specific surface area increased in the beginning, reached a maximum after a few hours, and then decreased slowly, while the pore volume increased continuously from the beginning. Figure 3 shows the change in the specific surface area and the total pore volume as a function of the temperature of the reaction for 2 h. The specific surface area increased from 10 °C, reached a maximum at about 100 °C, and then decreased gradually, while the pore volume increased continuously from 10 °C. These increases in the surface area in Figs. 2 and 3 can be explained reasonably as will be done below. Silica hydrogel is an aggregate of fine primary particles of silica loosely chained to each other with a small number of contact points per particle (coordination number). When aging is insufficient, the dehydration of water produces a xerogel with a very high packing density and with a high coordination number, since the strength of the contact points is weak and the reorientation of primary particles is easy. However, a mild hydrothermal treatment of hydrogel below 100 °C, such as is shown in the above experiments, can make the contact points stronger and does not make the size of primary particles larger, because silicic acid migrates from the convex surface of the particle to the points of contact with a concave shape and fills these narrow gaps. This produces stronger interparticle bonds than those before aging. These strong bonds make it difficult for the primary particles to reorient when hydrogel is dried, and thus give rise to a lower packing density and a smaller coordination number of xerogel. The number of coordination can be estimated from the packing density of xerogel, assuming this xerogel to be a mono-

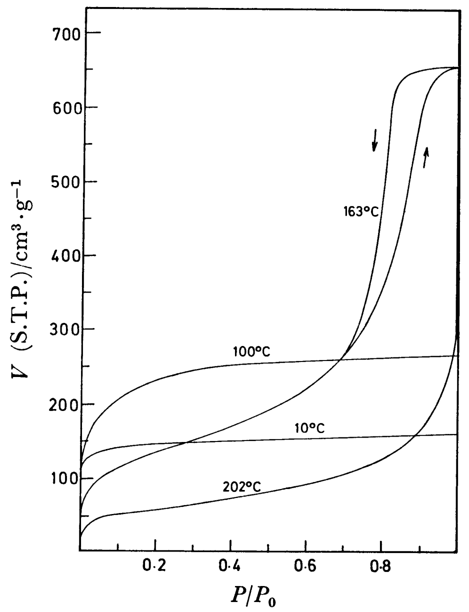


Fig. 1. The nitrogen adsorption isotherms of silica gel hydrothermally treated at various temperatures for 2 h.

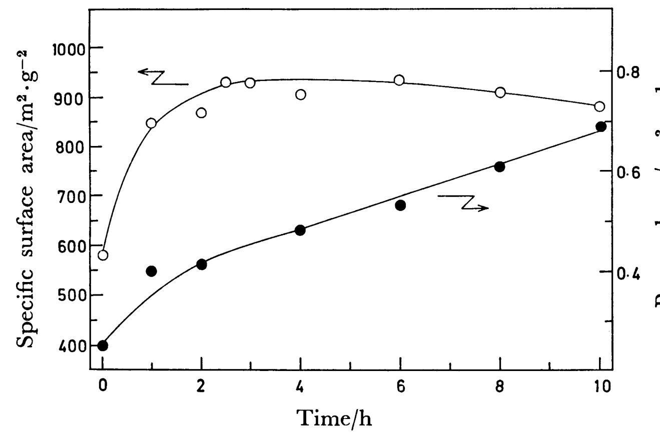


Fig. 2. The specific surface area and the pore volume of silica gel versus the time of hydrothermal reaction at 100 °C.

dispersed system of primary particles with a density of about 2.2 g/cm^2.[5] For example, the hydrothermal reaction at 10 °C and 100 °C for 2 h gives coordination numbers of about 9 and 6 respectively.

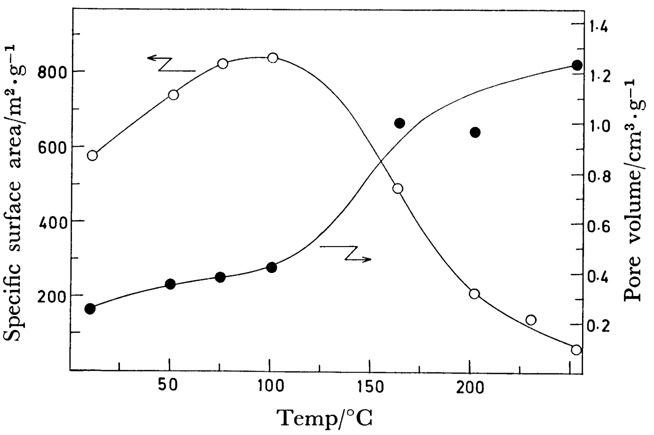


Fig. 3. The specific surface area and the pore volume of silica gel versus the temperature of hydrothermal reaction for 2 h.

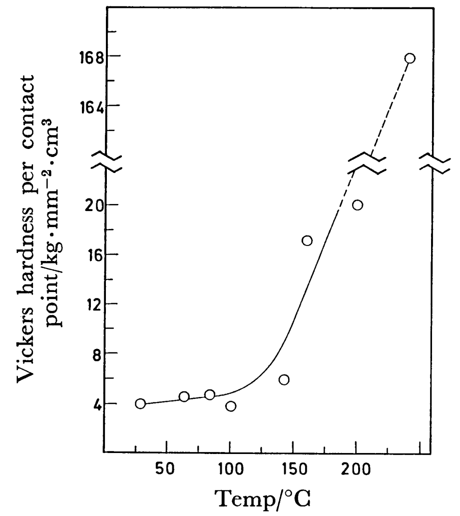


Fig. 4. The Vickers hardness per interparticle bond as a function of hydrothermal temperatures.

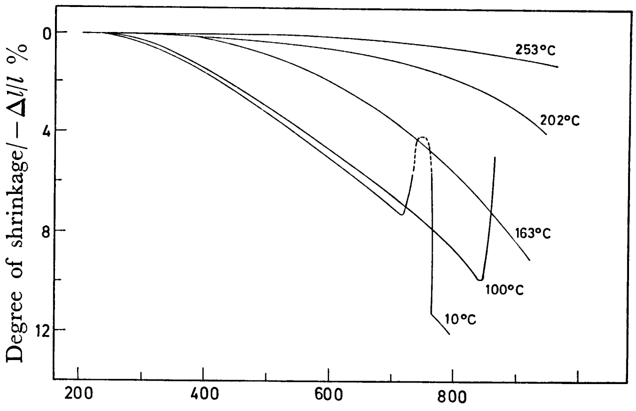


Fig. 5. The curves of thermodilatometric analysis of silica gel hydrothermally treated at various temperatures.

The reinforcement of these interparticle bonds by aging is reflected in the increase in the mechanical strength of silica gel as a bulk. Figure 4 shows the values of the strength of the silica gel per bond against the hydrothermal temperature, values obtained from the Vickers hardness (the pressure, kg/cm^2, neccessary to make a tiny hole of a known cross-section area on the flat surface of a specimen using a small diamond piece with a quadrangular pyramidal shape) divided by the total coordination number per unit of volume of the silica gel. In this figure, the bond strength increases as the hydrothermal temperature is raised. Another example of the increase in the bond strength is the thermodilatometric analysis of this material in Fig. 5, the experimental details of which were described elsewhere.[6] This figure shows that the degree of shrinkage of silica gel by heat treatment was smaller for materials of a high hydrothermal temperature, because the deformation or the shrinkage of bulk

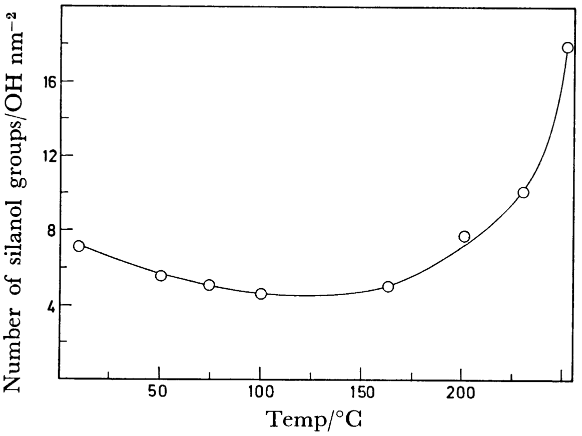


Fig. 6. The number of OH groups per nm^2 of silica gel hydrothermally treated at various temperatures.

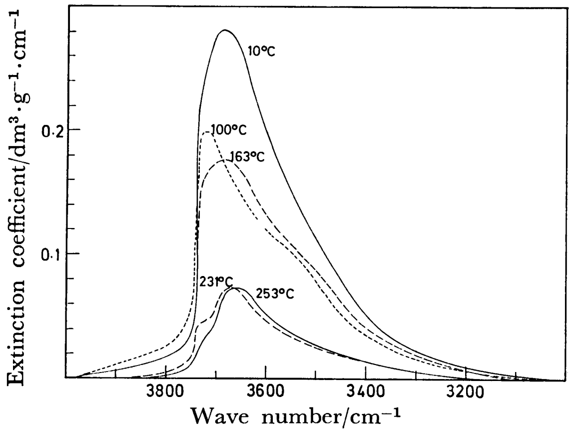
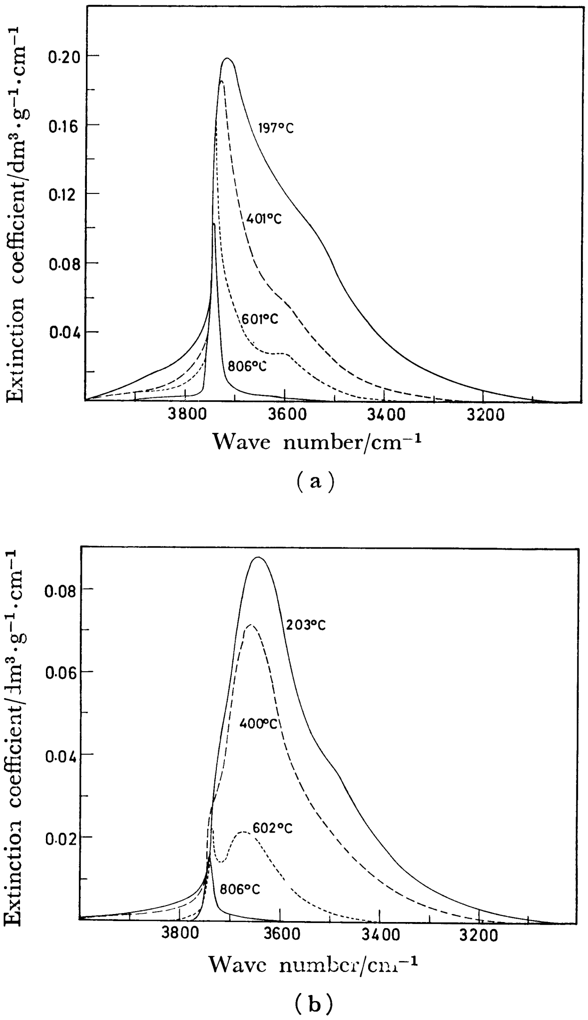


Fig. 7. The infrared spectra of OH stretching fundamental vibration of silica gel hydrothermally treated at various temperatures.



(a)

(b)

Fig. 8a and 8b. The changes of OH bands by heat treatment of silica gel hydrothermally treated at 100 °C and 250 °C, respectively.

structure by sintering would be smaller for materials with stronger interparticle bonds.

The gaps around the contact points between primary particles are so narrow that molecules such as nitrogen and water can not be adsorbed on a certain area around these points, depending upon the size of the molecules to be adsorbed. This area, which can not be measured by the adsorption of nitrogen gas, amounts to a considerable portion of the total surface area of the primary particles when these primary particles are small and possess a large number of coordination. Therefore, the specific surface area, as measured by the gas-adsorption method, will be generally larger for the materials having a smaller number of coordination when the diameters of the particles are equal, which seems to be true in case of mild hydrothermal treatment.

Figure 6 shows the number of OH groups per nm^2, which is obtained from the weight loss of the silica gel during heating between 180 °C (the temperature of the dehydration of adsorbed water) and 1200 °C divided by the specific surface area, as measured by the B. E. T. method using nitrogen gas. In this figure, the surface OH density is relatively larger for materials treated below 100 °C than those between 100 °C and 160 °C, because the specific surface area used for this calculation is smaller than the total surface area for the material hydrothermally treated at a lower temperature, as has been discussed in the above section. Above 100 °C, where the B. E. T. specific surface area approaches the total surface because of the decrease in coordination number, the OH density becomes smaller than 5. Surprisingly high values of OH density were obtained above 200 °C; the reason for this will be discussed below in terms of infrared spectroscopy.

Figure 7 shows the infrared spectra of the OH stretching vibration of silica gel treated hydrothermally at various temperatures for 2 h. The shapes of these OH bands changed markedly as the hydrothermal temperature was raised. As was shown in an earlier paper,[3] these bands can mainly be resolved into three component bands with absorption maxima at about 3750 cm^{-1}, 3670 cm^{-1}, and between 3500 and 3300 cm^{-1}; those maxima can be assigned to free OH groups, weakly perturbed OH groups, and strongly hydrogen-bonded OH groups respectively. As the hydrothermal temperature was raised, the intensity of free and strongly hydrogen-bonded OH components became smaller in comparison with the weakly perturbed components. The intensities and shapes of these OH bands of various

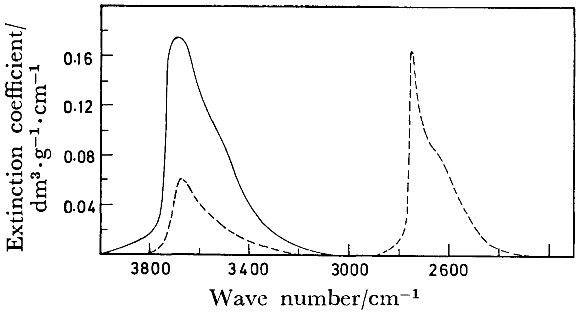


Fig. 9. The change of OH band of silica gel hydrothermally treated at 163 °C by the isotope exchange reaction by the absorption-desorption cycles of 20 times of heavy water. The full and the dotted lines show the absorption bands before and after the isotope exchange, respectively.

samples changed by heat treatment *in vacuo* as is shown in Figs. 8a and 8b. The OH band of silica gel hydrothermally treated at 100 °C in Fig. 8a became sharper when the temperature of heat treatment was raised, because of the decrease in the intensity of the strongly hydrogen-bonded component. By the heat treatment at 800 °C, the free OH component was clearly seen besides a small weakly perturbed component. On the other hand, the OH band hydrothermally treated at 250 °C in Fig. 8b obviously has two components at 3750 and 3670 $\mathrm{cm^{-1}}$ upon heat treatment at 600 °C, but it has almost no component below 3600 $\mathrm{cm^{-1}}$. After this sample was heated at 800 °C, there remained only 3750 $\mathrm{cm^{-1}}$ component. The decrease in the strongly hydrogen-bonded OH component against the hydrothermal temperatures seems to be roughly parallel to that of the coordination number. Therefore, it seems reasonable to assume that most of these strongly hydrogen-bonded OH groups lie on the surface around the contact points and contribute to the formation of interparticle bonds.

The intensity of the 3670 $\mathrm{cm^{-1}}$ band increased as the temperature and the time of hydrothermal reaction were increased, and the shape of this component became clearly visible at higher hydrothermal temperatures. This component can also be made visible by a sufficient isotope exchange of protons of OH groups by the adsorption of heavy water, as is illustrated in Fig. 9. A similar result was reported by Abramov and others.⁷⁾ Figure 9 shows the infrared spectra after a sufficient isotope exchange of the OH band of silica gel hydrothermally treated at 163 °C. According to our qualitative observation, the 3750 $\mathrm{cm^{-1}}$ component seems to shift to 2750 $\mathrm{cm^{-1}}$ most quickly; this seems to suggest that the sites of the free OH groups are on outer convex surface, so that heavy water can be adsorbed there directly. The exchange rate of protons of the strongly hydrogen-bonded OH groups seems to be slower. This indicates that these OH groups lie on the surface near the contact points where heavy water can not be directly adsorbed, and that the H–D exchange can be carried out by the diffusion of protons and deutrons through hydrogen-bond chains of the OH groups. The exchange equilibrium was almost attained after about 20 cycles of the adsorption-desorption processes of heavy water; there remained only an OH band at about 3670 $\mathrm{cm^{-1}}$. This behavior suggests that these OH groups are on the surface inside closed pores that have been produced by hydrothermal treatment, by which not only the concave surfaces at the contact points, but also small openings surrounded by a few contact points of a dense aggregate of primary particles are filled with a siloxane net work. Not even the heavy-water molecules can migrate into these closed pores.

The reason for the weak perturbation of these inner OH groups might be that the OH vibration is perturbed by a local dielectric field, which seems to be rather strong inside these small closed pores.⁸⁾ The intensity of the 3670 $\mathrm{cm^{-1}}$ component grew larger when the hydrothermal temperature was raised, as can be seen in Fig. 7. This suggests an increase in the area of the surface in the closed pores or an increase in the number of closed pores. There are two more pieces of evidence for the existence of the closed pores. By impregnating this material with impurities such as the sodium cations, the temperature of sintering is considerably lowered; even the free OH band disappears above about 800 °C, while the 3670 $\mathrm{cm^{-1}}$ band remains as it was, or its intensity even increases a little.²⁾ This phenomenon was interpreted as resulting from the occurence of closed pores by high-temperature sintering. Another example is the ion-exchange experiment of the OH groups of this materials with $\mathrm{Co^{2+}}$ ions.⁹⁾ After immersing the silica gel being hydrothermally treated at about 150 °C in a saturated aqueous solution of cobalt(II) acetate, the OH groups which were not ion-exchanged were mainly inner OH groups, together with a small part of the strongly hydrogen-bonded OH component.

The surface area inside these closed pores can not be measured by the nitrogen-adsorption method, since nitrogen molecules can not easily migrate into these pores, although the amount of OH groups can be measured by means of the weight loss of this material, as has been mentioned before, at 1200 °C, at which temperature all the OH groups including those inside the closed pores can be dehydrated by the explosion of closed pores at high temperatures, as has been mentioned elsewhere.²⁾ Upon hydrothermal treatment at high temperature, the fraction of the surface area inside the closed pores compared to that of the total surface increases greatly; this proves the extraordinarily large values of the OH density of silica gel at high hydrothermal temperatures. Exactly the same behavior was observed during the sintering process of this material, in which the surface area dropped to very low values, while the OH density increased highly at the same time, accompanied by the production of closed pores.²⁾ The amount of these inner OH groups can be estimated from the intensity of the 3670 $\mathrm{cm^{-1}}$ band after sufficient isotope exchange of OH group, assuming that the absorption intensity per OH group is the same for all three types of OH groups, although the degree of perturbation is different for these OH vibrations. The results of this estimation, together with the other properties of this material are shown in Table 1. In Column 5 of this table, the number

Table 1. The surface areas and the number of OH groups per nm^2 of silica gel hydrothermaly treated at various temperatures

Temperature of hydrothermal reaction, °C	Specific surface area, m^2/g	Number of OH groups per unit weight, 10^{21}/g	Ratio of H-D exchangeable OH groups to total OH groups	Number of outer OH groups, 10^{21}/g	OH Density of outer surface per nm^2	Total surface area, m^2/g
10	579.5	4.13	0.85	3.5	6.1	1033
50	742.1	4.13	0.84	3.5	4.7	1033
75	825.4	4.20	0.81	3.4	4.1	1050
100	839.4	3.83	0.76	2.9	3.5	958
163	495.1	2.48	0.73	1.8	3.7	620
202	214.3	1.67	0.43	0.73	3.4	418
230.5	146.6	1.49	0.27	0.40	2.7	373
253.0	63.5	1.13	0.26	0.29	4.6	283

of OH groups which can be exchanged with OD groups can be estimated from the intensity of the total OH band subtracted by that of the inner OH band. The surface densities of outer OH groups can be calculated from these values in Column 5, divided by the outer surface area, which is nearly equal to the B. E. T. specific surface area in Column 2; the results are shown in Column 6. These values of the OH surface density are less than 4/nm^2 above 100 °C, where the surface area around the particle contacts is negligible, but are more than 4 below 100 °C, where the number of coordination is so large that the area around these points can not be neglected. It is interesting to see that the OH density of non-porous aerosil is about 3.8/nm^2, which is almost equal to the values shown in the table.

If the bulk siloxane structure of primary particles of silica gel was homogeneous everywhere inside the particle, the surface density of OH groups would be the same all over the particle surface. Therefore, it seems possible to obtain the total surface areas of the primary particles of this material by dividing the number of the total OH groups per unit of weight in Column 3 of Table 1 by the surface OH density of 4/nm^2. The total surface areas thus estimated are shown in the last column of Table 1. It is interesting to see that the total surface area below 100 °C is nearly equal to that calculated by taking the area around the contact points into account, as will soon be reported elsewhere.$^{10)}$ The number of OH groups, 4/nm^2, obtained here is also in good agreement with that obtained from the study of the heat of the immersion of silica gel thermally treated under various conditions.$^{11)}$ The pore structure of silica gel proposed in this investigation is in fair agreement with the view given by Barby.$^{12)}$

Conclusion

The surface OH groups of silica gel are found to consist mainly of three types; the free OH groups on the outer convex surface exposed to the molecular adsorption and with an infrared absorption band at about 3750 cm^{-1}, the inner OH groups on the concave surface inside the closed pores at about 3670 cm^{-1}, and the strongly hydrogen-bonded OH groups on the surface around the contact points between primary particles with a broad absorption band at about 3500—3300 cm^{-1}. The pore structure and its change upon the hydrothermal and thermal treatment seem to influence the relative concentrations of these three types of OH groups of silica gel.

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