BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(6), 1533—1534 (1974)

The Direct-current Conductivity of Silica Gel[†]

Masa-aki MUROYA and Seiichi KONDO*
Osaka Electro-Communication University, Neyagawa-shi, Osaka 572
* *Osaka University of Education, Tennoji-ku, Osaka 543*

(Received June 16, 1973)

Synopsis. The study of the effect of heat-treatment on the direct-current conductivity of silica gel showed that the conductivity changed in response to the dehydration of the adsorbed water and of various kind of silanols. The temperatures of dehydration by this experiment seems to coincide with other experiments such as IR spectroscopy.

The study of direct-current conductivity is useful in investigating the surface of a colloid such as high specific-surface-area silica, since a major part of the measured current is considered to be due to the surface current in such material[1)] and, since the behavior of the charge carriers lying on its surface may play a central role in the conductivity. According to the recent studies of this material, several types of silanol groups dehydrate from the surface in various temperature ranges.[2,3)] Therefore, the thermal behaivor of these silanol groups is expected to influence the conductivity of this material sensitively. Similar points of view have been presented in several investigations of the conductivity of silica gel.[4,5)] In this kind of experiment, however, such impurities as alkali ions generally have a marked influence not only on the drastic thermal changes of the properties of silica gel,[6)] but also on the values of the conductivity. Therefore, the thermal effect of the surface conductivity of silica gel was studied in this investigation using high-purity silica gel with high-purity gold electrodes.

Experimental

Material. Ethyl orthosilicate was hydrolyzed to silica sol and gelled on a plastic plate. When the hydrogel thus formed was dried in air, a glass-like plate about 1 mm thick and about 3 cm^2 in area was obtained. The organic substances remaining in the silica gel were oxidized by hydrogen peroxide. No alkali and alkaline earth impurities were detected within our range of experimental error (about ±1 ppm) in the case of sodium ion. The BET N_2 specific surface area of this sample, S_A, was about 650 m^2/g, and the pore volume was 0.33 ml/g.

Conductivity Measurement. Gold films about 99.999% pure and of 10^{-5} cm thick, and 0.28 cm^2 in area were vacuum-deposited as the electrodes on the same plate which had been sufficiently preheated at about 150 °C and 10^{-5} Torr. This sample was then placed between platinum electrodes placed in a furnace, whose temperature range was from room temperature to 650 °C under a vacuum of 10^{-3} Torr. All these parts were then placed in a vacuum cell made of quartz and Pyrex glass. The applied voltage was mostly 1.000±0.001 V, which was sufficiently low enough to maintain the Ohm's law, and the error of the current measurement was about ±1% or 10^{-3} A. More details of the experiment will be described elsewhere.[7)]

According to a simple pore structure model of silica gel in which all the pores lie uniformly in the directions parallel to x, y, and z axes (the z axis is the direction of the electric field, and the x and y axes are perpendicular to the z axis), one third of the total pores in the z axis, which has one third of the total surface area, contribute to the surface conductivity. With this model, the value of the surface conductivity, σ_s, can be calculated as follows;

$$\sigma_s = \frac{l^2}{r}\cdot\frac{3}{S_A\cdot\rho\cdot v} \qquad (\text{ohm}^{-1})$$

where l is the electrode distance; r, the resistance; ρ the apparent density, and v, the volume between the electrodes. The experimental error of the relative value of the resistance was ±1%, that of the absolute value was about ±5%, and the minimum observable value was about 1×10^{-21} ohm^{-1}.

Results and Discussion

Figure 1 shows the relation between the surface conductivity, log σ_s, and the reciprocal temperature of the heat-treatment of silica gel. The surface conductivity increased gradually and irreversibly when the heat-treatment temperature was elevated in the range from room temperature to about 160 °C, as is shown by the white circles in the figure. When this sample was then cooled from 160 °C, the conductivity decreased linearly along a different route from the original one, as is shown by Curve *a* of this figure. With this thermal history, the conductivity change was reversible along Curve *a*. This difference seems to be caused by the desorption of adsorbed water. From

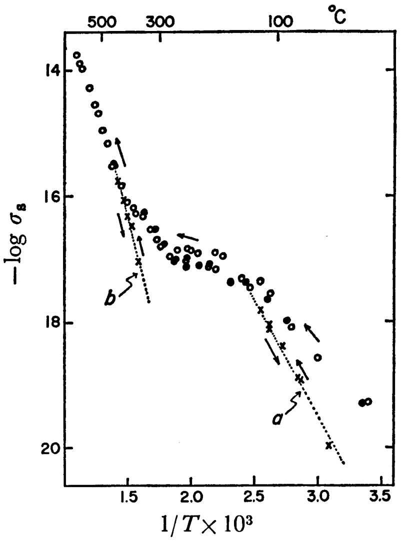

Fig. 1. Log σ_s (the surface conductivity) *versus* reciprocal temperature relation of silica gel.

[†] Presented at the 26th annual meeting of the Chemical Society of Japan, 1972.

about 170 °C, at which the desorption of water was completed, to about 350 °C, the conductivity curve deviated largely from linearity. As is shown by black and white circles in this figure, the conductivity in this range showed an analogous thermal behavior, but has different absolute values from sample to sample. On the other hand, the infrared study[8)] revealed the existence of four types of silanols (b, c, d, and e), and the b-type silanol, whose absorption band is the largest and has the maximum at 3260 cm^{-1}, starts to decrease at 170 °C and disappears at 350 °C. Therefore, the dehydration of this b-type silanol may be responsible for the large decrease in the conductivity. From about 350 to 650 °C, the conductivity increased when the heating temperature was elevated. When the sample cooled after heating at about 450 °C, for example, the conductivity decreased with a different temperature coefficient from that of the heating curve along reversibly Curve *b* in Fig. 1, while it increased reversibly within the range of Curve *b* when the sample was heated. The reason for this difference seems to be that the c-type silanol, which has the 3470 cm^{-1} absorption band, begins to dehydrate at 350 °C. Although still more silanol groups stable at temperatures higher than 650 °C are known to exist,[2,3,8)] measurements at such high temperatures in a vacuum were not possible in the present experiment.

References

1) J. J. Bikerman, "Physical Surfaces," Academic Press, New York (1970), p. 428.

2) S. Kondo, *Hyomen*, **10**, 321 (1972).

3) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, London (1966).

4) A. Soffer and M. Folman, *Trans. Faraday Soc.*, **62**, 3559 (1966).

5) J. H. Anderson and G. A. Parks, *J. Phys. Chem.*, **72**, 3662 (1968).

6) S. Kondo and M. Muroya, This Bulletin, **43**, 3453 (1970).

7) M. Muroya and S. Kondo, *Rept. Osaka Electro-Communication Univ.*, **10**, 1973.

8) S. Kondo, M. Muroya, and K. Fujii, This Bulletin, **47**, 553 (1974).