The Dehydration of Surface Silanol on Silica Gel

Seiichi KONDO* and Masa-aki MUROYA**

* *Osaka University of Education, Tennoji-ku, Osaka*
** *Osaka Electro-Communication University, Neyagawa, Osaka*

(Received February 23, 1970)

The thermal behavior of surface silanol groups on silica gel has been extensively studied.[1-3] Several authors have suggested various models, including the quasi-crystalline structure of the silica substrate, for the configuration and the dehydration reaction of free and hydrogen-bonded silanol groups. If the dehydration reaction occurs, the heat of reaction can be expected. In the present paper, some experimental findings derived by means of differential thermal analysis and thermogravimetric analysis are reported.

Silica gel was washed until the remaining sodium impurity became about 70 ppm of Na_2O. The presence of less than 100 ppm of the Na ion was shown to have a negligible effect on the thermal properties of silica gel.[4] The BET N_2 specific surface area of this material was 690 m^2/g.

The simultaneous measurements of DTA and TGA were carried out by means of two apparatuses, a Rigakudenki Co. Model 8001 CSL and a Shimadzu Model MTG-11. The sensitivities of the former instrument were ± 0.005°C and ± 0.02 °C using Chromel-Alumel and Pt-PtRh thermocouples respectively for DTA and ± 0.03 mg for TGA. About 30 mg of a powdered sample was heated in air in a shallow-dish-type platinum cell, using α-Al_2O_3 as the reference material, at a heating rate of 10°C and 20°C per minute.

Four endothermic DTA peaks, accompanied by four steps of weight decreases in the TGA curves and two exothermic DTA peaks, without any observable discontinuity in the TGA curves, were obtained in the range from room temperature to 1100°C, as shown in Fig. 1.

The largest DTA peaks at 150°C with the biggest weight decreases is obviously due to the desorption of adsorbed water. Three small peaks, 1, 2, and 3, at about 200, 400, and 500°C, and the corresponding small weight decreases are the facts newly found in this investigation. The pure sample which had preliminarily been heated at 570°C for six hours and then exposed to humid air with a 90% relative humidity for six hours showed smaller DTA and TGA changes at the same temperatures as that above. The ratio of these changes to each other was roughly equal to those obtained without preheating.

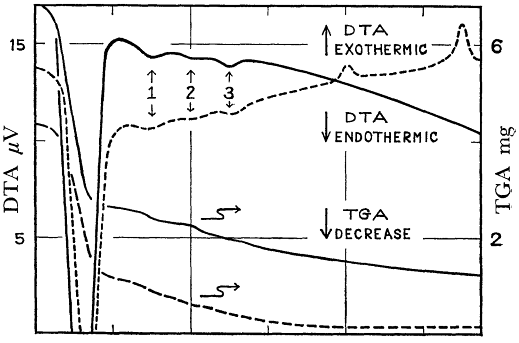

Fig. 1. DTA and TGA curves of silica gel. Full and dotted lines show pure and impure samples containing 70 and 800 p.p.m. Na_2O respectively. Sample weight was 30 mg and heating rate was 20°C/min in air.

According to the preliminary test of the infrared spectroscopy in this laboratory, four absorption bands were observed in the O–H stretching vibration region, *i.e.*, at 3230, 3460, 3620, and 3750 cm^{-1}. These bands disappear, one after another, in the order from lower to higher wave numbers (except the 3750 cm^{-1} band assigned to the free silanol group) by successive heating at about the same temperatures where DTA peaks disappear. Therefore, it seems reasonable to relate the DTA peaks 1, 2, and 3 to the bands at 3230, 3460, and 3620 cm^{-1} respectively. These considerations suggest the existence of four species of silanol groups, one free and three hydrogen-bonded silanol species. According to the quasi-crystalline structure model,[2] the surface of the silica particle might have various kinds of planes, which may give rise to various types of silanol groups, similar to the crystal planes, such as (100), (110), (210) and (211), of cristobalite or similar planes of other silica crystals. The present results seem to support this theory.

No endothermic DTA peaks were found above 600°C. Two exothermic peaks, shown in Fig. 1 on samples impregnated with some metallic salts, were interpreted as the heats of crystallization to cristobalite at 800°C and to quartz or tridymite at 1000°C.[4]

---

1) McIntosh, "Dielectric Behavior of Physically adsorbed Gases," Marcel Dekkar, Inc. New York (1966).

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

3) J. B. Peri, *J. Phys. Chem.*, **70**, 2937 (1966).

4) S. Kondo and M. Muroya, presented at the 22nd annual meeting of the Chem. Soc. Japan, 1969.