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NOTE

Bulk-like Siloxane Links on Silica Surface

A progressive increase in the intensity of the SiOSi bending band at 470 cm^{-1} in the DRIFT spectrum of silica gel is recorded upon heating in the temperature range 100–400°C. This increase in intensity is attributed to surface siloxanes formed due to condensation of surface hydroxyls which were necessarily too near to each other. Since the newly formed siloxanes showed their bending mode at the same frequency as that of the siloxanes in the bulk, both types of siloxanes are considered similar. © 1995 Academic Press, Inc.

Key Words: **silica gel; siloxane links; dehydroxylation; DRIFTS.**

INTRODUCTION

It is concluded that with mild heating (<400°C) adjacent OH groups on silica surface dehydroxylate to liberate water and form symmetrical siloxane-sites. These are different in reactivity from the sites formed at higher temperatures (>400°C) (1). In the latter case, spectral evidence was presented and considered to result from unsymmetrical siloxane sites (bands at 908 and 888 cm^{-1} and shoulder at 940 cm^{-1}). On the other hand, although it is recognized that rehydration is completely reversible up to 400°C (2, 3), no direct evidence was given to indicate the formation of symmetrical siloxanes. It seems that the recognition of the symmetrical sites is more or less rational, while because, in the case of unsymmetrical sites, the corresponding features were outside the vibrational range associated with the bulk, corresponding spectral reasoning was feasible. A careful perusal of the literature shows that a few studies (1, 4, 5, 6) were extended to the frequency region below 1000 cm^{-1} and even below 400 cm^{-1} (7). None of these studies, however, gave any attention to the region 500–400 cm^{-1} where the band at 470 cm^{-1}, due to the bending mode of SiOSi, appears (8). This attention is given in the present note which introduces the DRIFT spectra (4000–3200 & 2000–400 cm^{-1}) of silica gel heated in air in the temperature range 100–400°C. The upper limit of this range was chosen on the basis that the unsymmetrical siloxanes begin to form only upon heating at temperatures higher than 400°C (1).

EXPERIMENTAL

The silica gel used was a Kieselgel 60 (Merck) with 450 m^2/g BET area and 0.040–0.063 mm particle diameter. Heating was conducted in air for 6 h in the temperature range 100–400°C. Spectra were recorded at room temperature on a Nicolet 20SX Fourier transform infrared spectrometer as KBr pellets. The diffuse reflectances, R_s of the sample and R_r of the nonabsorbing KBr reference, were measured in the same conditions, and the reflectance was defined as $R = R_s/R_r$. The spectra were collected at a mirror velocity of 0.8 cm/s at a nominal resolution of 4 cm^{-1} after averaging 400 scans and were presented in Kubelka–Munk units, $F(R) = (1 - R)^2/(2R)$.

RESULTS AND DISCUSSION

Interesting spectral changes due to heating (100–400°C) (see Fig. 1) can be easily noted: (1) a consecutive increase, with no change in position, in the intensity of the band at 470 cm^{-1}, as inferred from its relative intensity if compared with the most intense band at 1200–1000 cm^{-1}; (2) the band around 800 cm^{-1} (ν_s SiOSi) became more symmetrical upon heating at 400°C; (3) the band at 970 cm^{-1} (ν Si-OH) shifted slightly to a higher frequency with a remarkable loss in intensity; and (4) the most intense band 1200–1000 cm^{-1} (ν_{as} SiOSi) showed no change neither in position nor in intensity. These last two events are well known (6, 9). It is to be noted that the spectrum of the nonheated sample (not shown) was practically indistinguishable from that of the sample heated at 100°C. The high-frequency region (4000–3200 cm^{-1}) reproduced the usual character of the band at 3743–3747 cm^{-1} due to isolated noninteracting hydroxyls. Furthermore, this indicates that at 100°C other types of hydroxyls are present; groups which are not too near to each other but are still able to form weak hydrogen bonding (3662 cm^{-1}) (7) and groups which are near each other so that they can form an extending domain of mutually perturbed hydrogen-bonded groups (3600–3200 cm^{-1}). These domains are depleted through condensation due to heating which resulted in the formation of

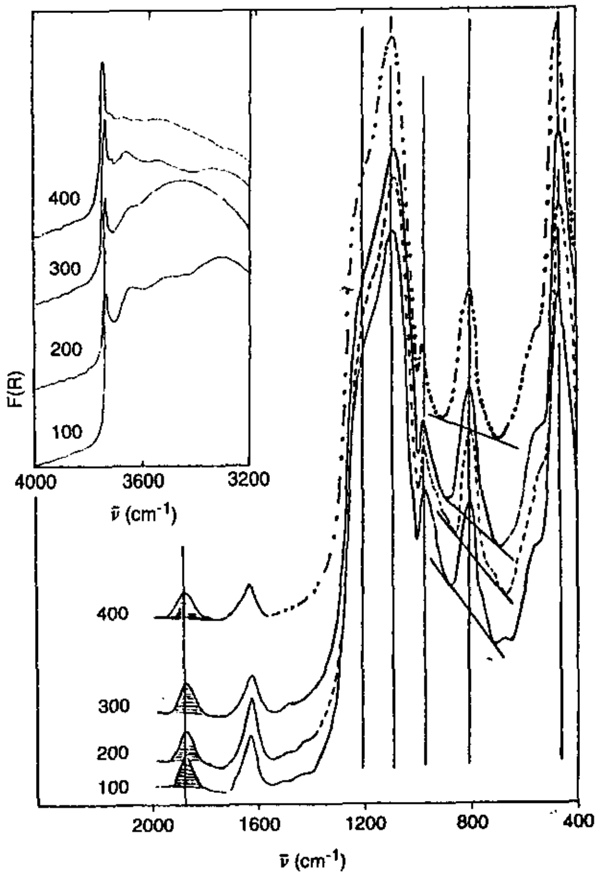

FIG. 1. DRIFT spectra of silica heated in the temperature range 100–400°C.

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isolated couples of hydrogen-bonded hydroxyls at 300°C as revealed from the bands at 3718 and 3535 cm^{-1} (1, 7, 10). Their isolated nature (band at 3718 cm^{-1}) is certainly due to their presence beside siloxane bridges that formed due to condensation of other couples of adjacent hydroxyls. We believe that these siloxanes are responsible for the increase, upon heating, in the intensity of the band at 470 cm^{-1}. Because they are similar to those in the bulk, they exhibited a similar bending mode. The fact that the newly formed siloxanes have shown their bending mode at the same frequency as that of the bulk indicates that they are characterized by a similar Si–O–Si angle (144°) and Si–O bond length (1.63 Å) (11). However, since the surface hydroxyls are not all equidistant, some different values of angles and bond lengths have resulted in the broadening which accompanies the increase in the band at 470 cm^{-1} (see Fig. 2). The inference is that the formation of the aforementioned siloxanes results from the condensation of the hydroxyls which are too near to each other and therefore can form strong hydrogen bonding. The decrease in this type of hydroxyls upon heating can be correlated with the decrease in absorption around 935 cm^{-1} (Fig. 2) due to νSi-OH of hydrogen-bonded hydroxyls (4). On the other hand, the decrease in perturbation due to hydrogen bonding can be correlated with the decrease in the broadness of the transmittance (700–500 cm^{-1}), a region attributed to δ(O-Si-OH) of both free and hydrogen-bonded hydroxyls (4). These last two spectral changes are behind the gain of symmetry of the band around 800 cm^{-1} (Fig. 2). Finally, we have to emphasize that the differences in the intensity of the band at 470 cm^{-1} (see Table 1) are not due to differences in sample mass as it can be seen from the constancy of the overtone bulk band (1860 cm^{-1}) (Fig. 1).

TABLE 1
Spectral Features of the Si-O-Si Bending Band (470 cm^{-1}) at Different Heating Temperatures

Temperature (°C)	Peak intensity × 10^3 (a.u.)	FWHM (cm^{-1})
100	77	70.4
200	84	73.0
300	130	75.3
400	154	75.3

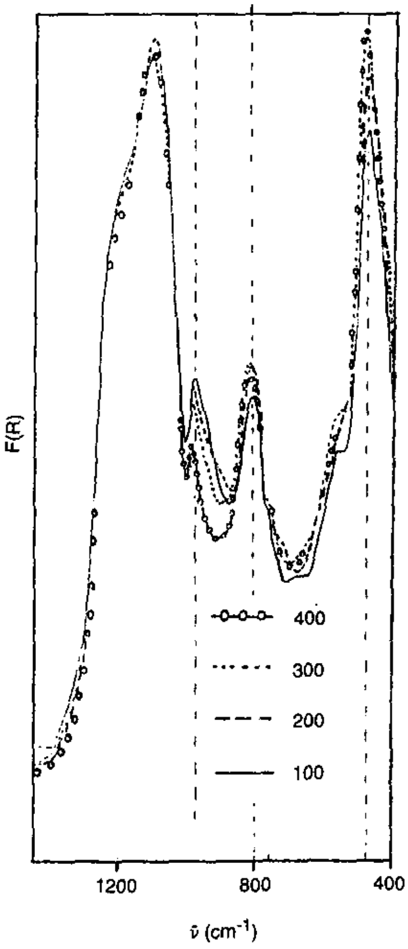

FIG. 2. DRIFT spectra (superposed) (1200–400 cm^{-1}) of silica heated in the temperature range 100–400°C.

The surface of a silica strongly depends on its manufacturing process, because surface groups are constrained by the three-dimensional network which backs up the surface. Therefore, the findings presented in this note may be related to the particular structure of silica gels, and the question of whether crystalline polymorphs or amorphous silicas of different origin will behave similarly merits further work.

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