Chemisorption of Molecular Hydrogen on Highly Dehydrated Silica

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STUDIES dealing with the thermal dehydration of silica gels have shown that the amount of water left on the surface of degassed silicas, mainly in the form of surface hydroxy-groups, is primarily a function of the outgassing temperature and not of the outgassing time.[1] The quasi-equilibrium concentration of surface hydroxy-groups is thus reached in a relatively short time at a given temperature, only minor changes occurring in that concentration on more prolonged outgassing. Thus, in our spectra in the O–H stretching region of a sample of Aerosil† only negligible modifications were observed in the intensity of the Si–OH band at 3747 cm.$^{-1}$ when the sample was outgassed for very long periods at 770°. Meanwhile, the material slowly developed an unexpected capacity of chemisorbing hydrogen at high temperatures.

Figure 1 shows the small band which was formed in the 2300 cm.$^{-1}$ region when hydrogen reacted with a silica pellet which had been degassed at 770° for 20 hr. After contact for 3 hr. with hydrogen at 680°, the band was centred at 2287 cm.$^{-1}$

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† Aerosil 2491/380, Degussa, Inc., Kearny, New Jersey.

(spectrum B, Figure 1); after a further 8 hr. at the same temperature, it was more intense and centred at 2294 cm.$^{-1}$ (spectrum C). No further modifications of the band were observed on exposing the sample to hydrogen, either for longer times (D), or at higher temperatures (E). Thus the chemisorption ability seems not a general property of the material, but of a few sites only.

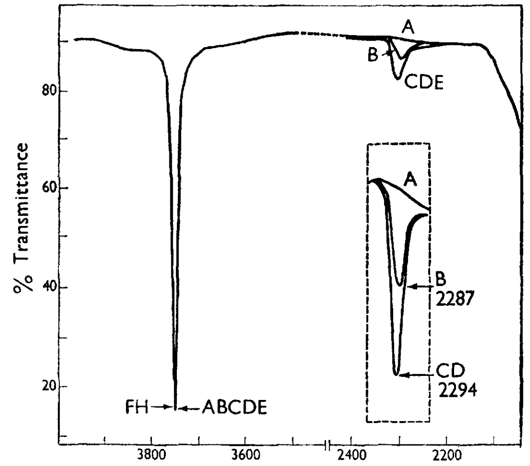

FIGURE 1. *Spectra of Aerosil. The sample was degassed at* 770° *for* 20 *hr.* (A), *exposed to* 40 *torr* H_2, *and heated at* 680° *for a total of* 3 *hr.* (B), 11 *hr.* (C), 30 *hr.* (D), *and at* 770° *for* 6 *hr.* (E). *The sample was then degassed at* 770° *for* 16 *hr.* (F), *heated in* 40 *torr* H_2 *at* 680° *for* 11 *hr.* (G), *degassed again at* 770° *for* 18 *hr.* (H), *and treated in* 42 *torr* H_2 *at* 680° *for* 12 *hr.* (J). *Portions of spectra* F *and* H, *and also spectra* G *and* J, *are not shown. The insert shows portions of spectra recorded at five-times ordinate expansion.*

The band near 2300 cm.$^{-1}$ was observed earlier[2] when surface methoxy-groups on silica were destroyed upon outgassing at high temperature. In a subsequent study[3] we assigned that absorption to the silicon–hydrogen stretching of $=SiH_2$ groups. Upon outgassing at high temperature, these could react with surface hydroxy-groups, leading to the formation of a surface radical. The latter would then chemisorb hydrogen at a temperature ranging from 25 to 500°, to form some $\equiv$Si–H groups absorbing at 2227 cm.$^{-1}$. On the basis of these previous results, we think that the present band at 2287–2294 cm.$^{-1}$ is formed through a mechanism,

$$\text{sites} + H_2 \longrightarrow SiH_2 \qquad (1)$$

but the nature of the sites still remains unknown.

If a hydrogenated sample was outgassed for long times at 770°, the SiH_2 groups were eliminated very slowly (Figure 2, spectra F, H), but not through the reaction with surface hydroxy-groups. In fact, the band at 3747 cm.$^{-1}$ did not appreciably change its intensity (Figure 1) and a 2-hr. reaction with hydrogen at 450° produced no band at 2227 cm.$^{-1}$. In that case the concentration of SiH_2 groups on the surface was probably too small;

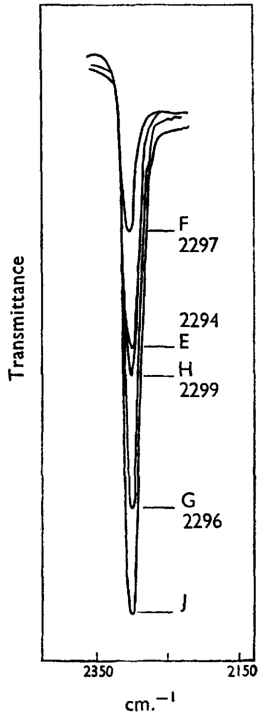

FIGURE 2. *Spectra of Aerosil in the* 2400—2100 *cm.*$^{-1}$ *region. These portions of spectra* (*of the sequence described in the legend to Figure* 1) *were recorded at five-times ordinate expansion.*

none, or very few of them, could interact with surface hydroxy-groups. We suppose that the elimination of the silane groups was merely the slow reverse of reaction (1), occurring first with the weaker and lower-absorbing groups, as shown by the shifted frequencies of the bands of spectra F and H of Figure 2. However, the major effect produced upon outgassing the sample at 770° for longer times was that more sites were formed which could react with hydrogen through mechanism (1). This effect, clearly shown in Figure 2, spectra G and J, confirms that the reactivity of the silica gel toward hydrogen was caused by some structural defects of unknown nature produced during the long activation at high temperatures.

Such phenomena have not previously been reported and, in view of the generally accepted inability of molecular hydrogen to react with silica, are unexpected and intriguing.

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[2] C. Morterra and M. J. D. Low, *Chem. Comm.*, 1968, 203.

[3] C. Morterra and M. J. D. Low, *J. Phys. Chem.*, submitted for publication.