

## Stable Si-H Groups on Silica Surfaces

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It is well known that silica surfaces can be methylated by reaction with methanol.<sup>1</sup> The surface Si-O-Me groups which are formed are stable and cannot be removed by pumping unless quite high degassing temperatures are used. However, when methylated Aerosil was degassed at 750°, the infrared bands due to the stretching vibrations of the methyl groups declined rapidly; simultaneously, a strong band appeared with a maximum near 2280 cm.<sup>-1</sup>. This is shown by the example in Figure 1. Spectrum A of a methylated Aerosil shows only the bands of the methoxy-group. After heating *in vacuo* for 1 min. at 750°, the 2280 cm.<sup>-1</sup> band appears (spectrum B) and grows on further heating (spectrum C).

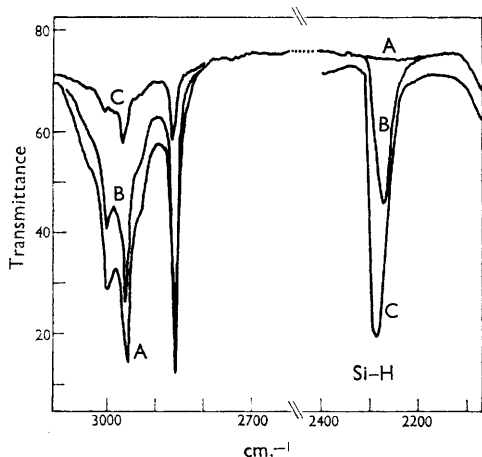


FIGURE 1. Infrared spectra of Si-H groups. A: methylated Aerosil. B: after heating at 750° for 1 min. in vacuo. C: after heating at 750° for 9 min. in vacuo.

We believe the 2280 cm.<sup>-1</sup> band to be caused by Si-H groups which were formed on the surface. This assignment is supported by the following observations. (a) The frequency of the band falls in the 2300—2100 cm.<sup>-1</sup> range found for Si-H

stretching frequencies.<sup>2,3</sup> (b) The reaction of Aerosil with CD<sub>3</sub>OD results in the formation of Si-OCD<sub>3</sub> groups; a spectrum is shown in Figure 2, trace A. Upon heating at 750°, the OCD<sub>3</sub> groups are destroyed and a strong band is formed near 1650 cm.<sup>-1</sup>. The ratio 2280/1650 = 1.38 is in good agreement with that expected for  $\nu_{\text{SiH}}/\nu_{\text{SiD}}$  for isotopic substitution. (c) The species absorbing at 2280 cm.<sup>-1</sup> is eliminated by heating the sample in oxygen; H<sub>2</sub>O is formed.

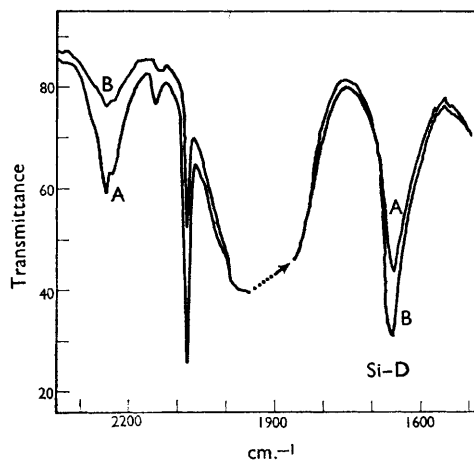


FIGURE 2. Infrared spectra of Si-D groups. A: Aerosil methylated with CD<sub>3</sub>OD after heating at 750° for 2 min. in vacuo. B: after heating at 750° for 11 min. in vacuo. The 1650 cm.<sup>-1</sup> band is superimposed on a broad absorption of the adsorbent.

The surface Si-H groups are stable in oxygen at 350°; *in vacuo*, they decrease only slowly at 750°. The mechanism of generation of the Si-H groups, and the properties of the latter, will be reported in detail elsewhere.

(Received, December 28th, 1967; Com. 1386.)

<sup>1</sup> E. Borello, A. Zecchina, and C. Morterra, *J. Phys. Chem.*, 1967, **71**, 2938; E. Borello, A. Zecchina, C. Morterra, and G. Giotti, *ibid.*, p. 2945 and references therein.

<sup>2</sup> E. A. V. Ebsworth, "Volatile Silicon Compounds," Macmillan, New York, 1963, pp. 17ff.

<sup>3</sup> L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, 1964, 2nd edn., pp. 334ff.