

Reactive Silica. Pyrolysis of Chemisorbed Silanes¹

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Summary When silica bearing certain chemisorbed silanes is heated to a high temperature *in vacuo*, the chemisorbed layer is disrupted and the surface of the silica is modified; surface =SiH₂ groups are formed and the silica surface becomes unusually reactive.

REACTIONS between various silanes and the surfaces of silicas and glasses have been the subject of numerous studies, partly because information could be derived about the nature and reactivity of surface silanols, and especially because silanes are useful as coupling agents for the fabrication of glass fibre-polymer composites and also as deactivating agents for the preparation of chromatographic supports. Some of the work has involved the use of i.r. spectroscopic techniques, so that surface species could be observed

directly.²⁻¹⁰ Here, we are concerned with the reactivity of the chemisorbed layer itself, and interest in reactive silica^{1,11,12} prompted us to investigate the stability of chemisorbed silane layers. Drastic changes were observed at temperatures somewhat higher than those used previously

I.r. spectra were recorded with Perkin-Elmer model 421 or 621 spectrophotometers.^{1,11,12} Highly degassed Cab-O-Sil or Aerosil silica powders were exposed to silane vapours at various temperatures from room temperature to 400°. The results obtained were in general similar to those reported previously or to be expected for the reaction of silanes with silanols, and will not be considered here. After the initial reaction had occurred, during which most or all surface silanols were removed, the i.r. cell was evacuated in order to remove excess of silane and volatile products.

The modified adsorbent was then heated *in vacuo* at sequentially increasing temperatures, spectra being recorded after the sample had cooled to room temperature.

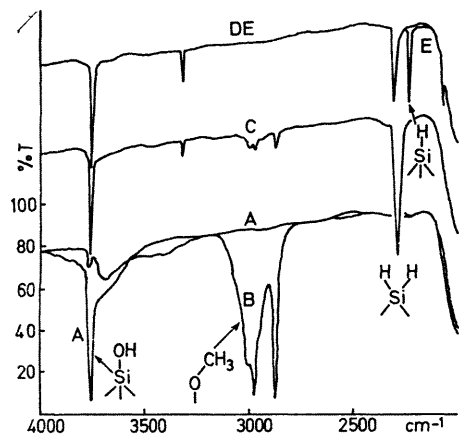


FIGURE 1. $\text{SiO}_2-(\text{CH}_3\text{O})_4\text{Si}$

A: SiO_2 sample after degassing for 3 h at 580° , exposure to H_2O vapour, followed by degassing for 3 h at 360° . B: After exposure to 10 Torr $(\text{MeO})_4\text{Si}$ at 295° for 45 min, cooling, and degassing for 15 min at 25° . C: After heating *in vacuo* for 30 min at 870° . D: After heating *in vacuo* for 24 h at 890° . E: After heating in 20 Torr H_2 for 1 h at 550° . The ordinates of spectra C, D, E are displaced.

Some results obtained with $(\text{MeO})_4\text{Si}$ are shown in Figure 1. A sample containing both isolated and bound surface silanols¹⁰ (spectrum A) was exposed to $(\text{MeO})_4\text{Si}$ vapour. Most of the hydroxy-groups were removed by this reaction, the spectrum then recorded (B) showing prominent C-H bands characteristic of $-\text{OMe}$. These declined rapidly when the sample was heated and were replaced by a sharp absorption band due to isolated silanols and a prominent band near 2290 cm^{-1} due to surface silane¹¹ (spectrum C). The $=\text{SiH}_2$ band declined on further degassing (spectrum D). The degassed sample then readily reacted with H_2 , there being a slight increase in the Si-OH band and also the growth of a pronounced band due to a second surface silane¹¹ (spectrum E). Similar results were observed with Me_3SiH . In each case the silica surface was modified and qualitatively exhibited the characteristics of 'Reactive Silica'.^{1,10,11}

More complex results were obtained with Me_3SiCl illustrated in Figure 2. When the silanized sample (spectrum A) was heated, the C-H bands declined rapidly and, in addition to a small Si-OH band and a prominent $=\text{SiH}_2$ band, some broad absorptions appeared in the $2350-2200\text{ cm}^{-1}$ region (spectrum B). The surface structures responsible for absorptions were removed by further

degassing (spectrum C). Treating the degassed adsorbent with H_2 then produced the $=\text{SiH}_2$ band (spectrum D) and a new band in the Si-H region near 2260 cm^{-1} (probably due

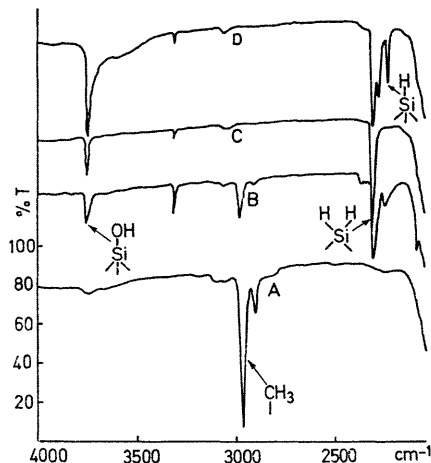


FIGURE 2. $\text{SiO}_2-(\text{CH}_3)_3\text{ClSi}$

A: SiO_2 sample after degassing at 810° for 20 h, exposure to 58 Torr Me_3SiCl at 400° for 15 h, and degassing for 2 min at 400° . B: After degassing at 810° for 30 min. C: After degassing at 860° for 20 h. D: After exposure to 87 Torr H_2 at 300° for 2.5 h. The ordinates of spectra B, C, D are displaced.

to a surface Si-H group); also, a prominent Si-OH band showing pronounced tailing was formed, in contrast to results obtained with 'Reactive Silica'. The Si-OH band was a doublet with maxima near 3748 and 3737 cm^{-1} . Further treatment with H_2 removed the 3737 and 2260 cm^{-1} absorptions, the Si-OH band increasing in intensity and being centred at 3747 cm^{-1} . The results suggest that the silica had become activated and capable of reacting with H_2 *via* at least two paths. Such activation did not occur when chemisorbed vinyltrichlorosilane was pyrolysed.

The various preliminary results, as well as other data on the pyrolysis of surface esters, suggest that a silica surface can become activated through the destruction of chemisorbed methyl and methoxy-groups or perhaps methyl radicals formed by the disruption of the chemisorbed species. The activation does not seem to occur if the surface group formed from chemisorbed alcohols or from silanes contains carbon only in the form of a chain of two or more carbon atoms.

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¹ For previous paper in the series 'Reactive Silica' see C. Morterra and M. J. D. Low, *J. Phys. Chem.*, 1970, **74**, 1279.

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