

The Porous Structure of Self-Supporting Pressed Silica Discs

I. Infrared Spectroscopic Studies

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Received June 7, 1968; revised September 30, 1968

Infrared spectroscopic studies of a range of silicas prepared from an Aerosil show that the 3650-cm^{-1} absorption band present in the spectrum of silica gels corresponds to the regions of interparticle contact within the gel matrix. A comparison of the spectra of powder silicas and the corresponding self-supporting pressed discs suggests that the latter possesses a microporous gel structure. The reactions of the silicas with heavy water and boron trichloride vapor show that it is not possible to differentiate at all accurately between bulk or internal hydroxyls and surface hydroxyls in silica gel structures by hydrogen/deuterium isotopic exchange methods using heavy-water vapor as the exchanging agent.

INTRODUCTION

It has long been realized that the adsorptive and catalytic properties of solid oxides are markedly dependent upon the nature and concentration of their surface functional groups. The most common type of surface species is the hydroxyl group or ion and infrared spectroscopic techniques have proved to be of great use in elucidating both the stereochemistry and coordination of such surface hydroxyls.

In order to obtain the required spectroscopic information it is necessary to use finely divided solids of relatively high specific surface area, which unfortunately "scatter" an appreciable quantity of the incident infrared radiation. This scattering, which is the result of optical interference, can be overcome by forcing the particles into contact, a procedure that is the basis of the pressed-disc technique as used by the great majority of workers in the field. The assumption involved, which is usually only implicit in such studies, is that the spectra so obtained may be interpreted as reflecting directly the surface structure of the corresponding powdered solid. That this basic assumption is invalid for some oxides has been known for some time (1, 2) and the initial objective of the present work was to

obtain quantitative information about the changes that occur in both the porous structure and the infrared absorption of oxide powders when they are pressed into self-supporting discs. Only at a later stage in the investigation was it realized that the results of the work were also relevant to other fields of study, in particular to the structure of oxide gels.

EXPERIMENTAL

The D_2O used for exchanging the surface hydroxyls to their deuterium analogues was Norsk Hydro (purity 99.7%). The boron trichloride was 99.5% pure. The purity and preparation of the silicas used in the present work has been described in detail elsewhere (3, 4). Briefly, the solids were examined as the original powders (from Degussa, Ltd.), for example, Untreated Aerosil Batch 3, U.A. 3. The "rehydrated" samples were prepared by slurrying about 2-3 kg quantities of the untreated oxide with pure water at 90°C for 3 hr (Rehydrated Aerosil Batch 2, R.A. 2) or at 95°C for 4-5 hr. (Rehydrated Aerosil Batch 3, R.A. 3), followed by filtration and drying in air at 120°C to constant weight. About 1 kg of this latter material was then heated to anneal it at 700°C for 48 hr, and this is designated R.A. 3/700.

In a similar way rehydration of R.A. 3/700 in pure water at 90°C for 3 hr leads to Rehydrated R.A. 3/700, viz., R.R. A3/700. (This rehydration procedure completely hydroxylates the surface and also markedly alters the appearance of the solid, increasing its bulk density by about one order of magnitude.) The mechanically pressed self-supporting discs are named according to the pressure in tons cm^{-2} used in their preparation from the powdered samples, e.g., R.A. 2/5. All the discs were prepared in a die that enabled the powders to be evacuated to 2×10^{-4} torr prior to pressing. Such a procedure, as previous studies (5) of the 1640- cm^{-1} region of the infrared spectrum have shown conclusively, ensured that all the O-H (O-D) absorption bands present in the infrared spectra were associated with hydroxyl groups and not molecular water (2, 5).

The spectra were recorded on a Perkin-Elmer 125 grating infrared spectrophotometer using a maximum spectral slitwidth of 3 cm^{-1} . The spectrometer was flushed with dry air throughout to eliminate any effects due to atmospheric water vapor. This was of particular importance when recording the spectrum of the powdered specimens. The samples under study were mounted in a cell of the type described elsewhere. The spectra of the powdered samples were obtained with the powder trapped between two Irtran 2 discs (chemically inert infrared transparent material from Eastman Kodak), separated by a thin gasket of aluminum foil. This assembly was held vertically against the flange in the center of the infrared cell by means of a weak spring (about 1 inch in diameter and consisting of approximately six turns of $\frac{1}{8}$ -inch copper wire). All the spectra presented correspond to the pseudo-equilibrium states of the solids under the treatment described in the figure legends. Thus they all represent the time-independent states of the samples concerned. Isotopic exchange of the samples was effected at room temperature by passing six separate doses of D_2O vapor at its room-temperature saturated vapor pressure into the infrared cell, the sample being evacuated at 10^{-4} torr for about 10 min between each pass.

RESULTS AND DISCUSSION

Electron microscopy and small-angle X-ray scattering have long since revealed (3, 10, 17) that silicas in general are composed of small primary crystallites possessing hydroxylated surfaces of the order of tens of angstroms in diameter aggregated into larger spheroidal particles of the order of hundreds of angstroms in diameter. A very illustrative and descriptive analogy may thus be drawn between such an aggregate and a soft fruit such as a raspberry or blackberry (18). A detailed consideration of the recent work of Davydov *et al.* (8) and some of our own recent studies has led us to realize that some of the difficulties encountered in interpreting experimental data obtained with silica substrates may be resolved by analysis of the data on the basis of this model.

1. Mechanical Pressure

Spectra (a) and (b) in Fig. 1 show the spectrum of U.A. 3, a fully hydroxylated silica, before and after treatment with D_2O vapor at room temperature. Spectrum (c) shows the effect of treating the deuterated sample with boron trichloride vapor at room temperature. The boron trichloride was used here as an eliminative molecular probe, to remove those hydroxyls situated on the exterior surfaces of the solid (?). In size the molecules increase in the order of D_2O , N_2 , and BCl_3 . Thus nitrogen is smaller than BCl_3 but larger than D_2O and was therefore used as the adsorbate in the physisorption studies rather than any other larger molecule.

The results show that the true surface groups are single hydroxyls associated with an absorption band at 3745(2755) cm^{-1} and the interacting hydroxyls which absorb around 3550(2620) cm^{-1} . The fact that there is an asymmetric residual band in the O-D region of spectrum (c) in Fig. 1, centered around 2690 cm^{-1} , shows that there are hydroxyl groups in the solid which are available for interaction and consequent exchange with heavy water although they are unavailable for interaction with a larger molecule such as boron trichloride. It follows that the results obtained from such isotopic exchange studies are not always able to

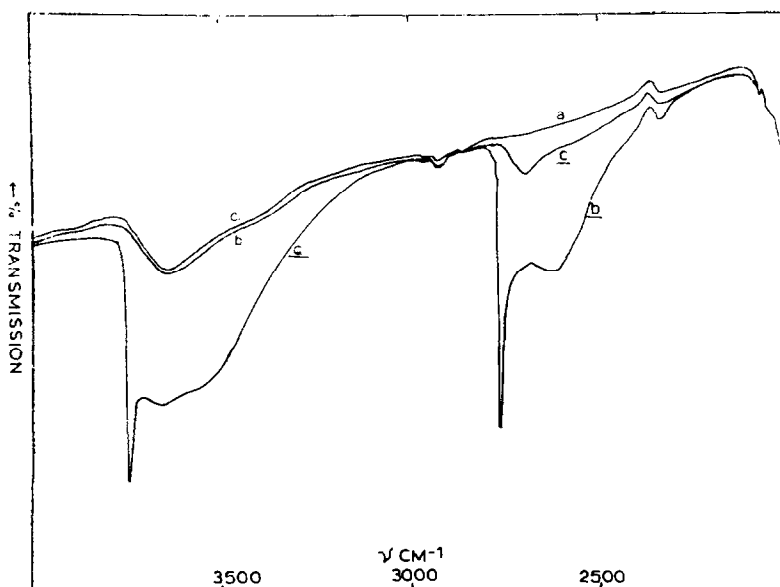


FIG. 1. The infrared spectrum of U.A. 3 powder after evacuation at 25°C at 10^{-4} torr (a); after exchange with D_2O vapor at 25°C followed by evacuation at 1×10^{-4} torr (b); and after treatment of the deuterated sample (b) with boron trichloride vapor at 25°C (c).

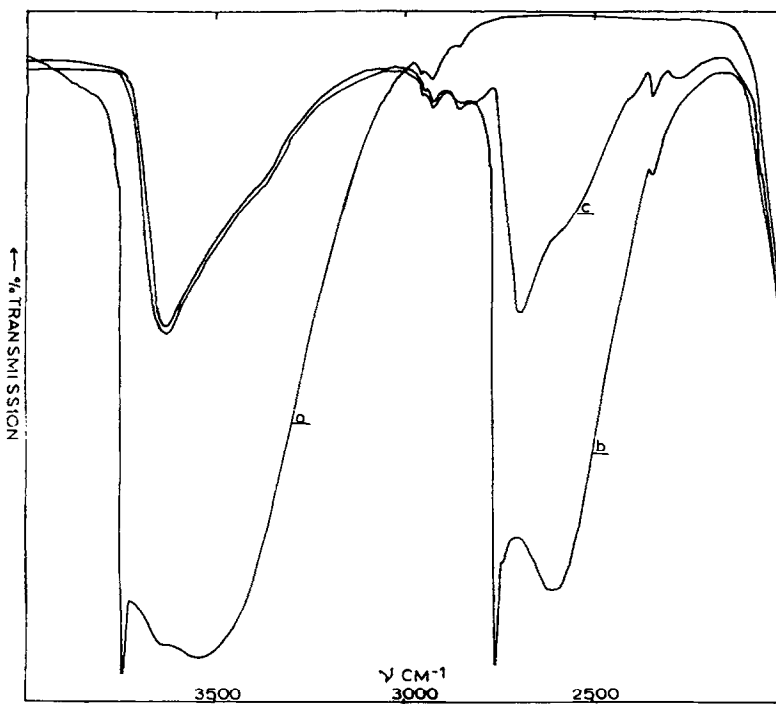


FIG. 2. Infrared spectrum of a U.A. 3/5 pressed disc after evacuation at 25°C at 10^{-4} torr (a); after treatment with D_2O vapor at 25°C followed by evacuation at 1×10^{-4} (b); and after treatment of (b) with boron trichloride vapor at 25°C (c).

TABLE 1
INTEGRATED AREA MEASUREMENTS^a

Sample	A ^a	B ^a	C ^a	D ^a	E ^a
R.A. 3/700	62	63	3	0	0
R.A. 3	732	560	210	210	120
U.A. 3	470	322	112	112	33
U.A. 3/5	2105	1520	441	441	304
R.R.A. 3/700	387	308	60	58	29
R.A. 2	2400	—	550	—	—

^a Column A: % Integrated absorption intensity of the total O-H absorption after evacuation at 10^{-4} torr at 25°C. Column B: % Integrated absorption intensity $\times 1.38$ of the total O-D absorption after exchange with D₂O vapor at 25°C followed by evacuation at 25°C at 10^{-4} torr. Column C: % Integrated absorption intensity of the residual O-H absorption after exchange with D₂O as described for column B. Column D: % Integrated absorption intensity of residual O-H absorption after treatment of the deuterated samples with BCl₃ vapor at 25°C followed by evacuation at 25°C at 10^{-4} torr. Column E: % Integrated absorption intensity $\times 1.38$ of the residual O-D absorption after treatment of the deuterated sample with BCl₃ as described for column D.

Note that for each of the samples the sum of the integrated intensities in columns B and C is equivalent to within about +5% of the integrated absorption intensity in column A.

differentiate meaningfully between surface and bulk hydroxyls (8). The integrated area measurements presented in Table 1 show that molecular D₂O can underestimate by as much as 100% the total concentration of bulk hydroxyls that are unavailable to adsorbing molecules larger than D₂O, even those that are still relatively small in absolute terms, such as boron trichloride which is effectively about 5-6 Å in diameter. For the adsorption of larger molecules such as hydrocarbons the discrepancy could of course be much larger.

The spectra shown in Fig. 2 correspond to the results obtained from a similar series of experiments using a U.A. 3/5 pressed disc. The only significant spectroscopic change induced by the pressing process is that the intensity of the residual absorption band at 3650(2690) cm⁻¹ is significantly increased, a change that has markedly altered the appearance of the whole spectrum compared to that obtained for the corresponding

powdered solid. The same effects are found with U.A. 2 when this sample is treated in the same way. Overall these results suggest that the species responsible for the absorption band at 3650 cm⁻¹ is associated with hydroxyl groups sited on adjacent silica particles and interacting at the interparticle junctions (12).

2. Hydrotensile Pressure

It has been known for many years (9, 10) that dry powders are aggregated if they are first slurried in an inert liquid phase and then redried. The aggregation is a consequence of the interfacial tensile forces drawing the initially discrete powder particles into closer contact as the liquid meniscus progressively shrinks into the interparticle interstices. It follows that an Aerosil silica that has been subjected to such a process should exhibit a marked increase in its absorption at 3650(2690) cm⁻¹ if the assignment given above for this absorption band is the correct one. Figures 3 and 4 show that this is the case for R.A. 2 and R.A. 3. The data shown in Table 1 [(E + C)/A] indicate more quantitatively that, compared to the powder U.A. 3, the intensity of the residual absorption band of R.A. 3 at 3650(2690) cm⁻¹ is a significantly greater percentage of the total initial hydroxyl absorption intensity.

3. Hydrothermal Treatment

Considering an aqueous dispersion of a finely divided insoluble solid, it may be argued from thermodynamic considerations that the "aggregated state" is more stable than the dispersed, and so aggregation will occur as a result of the tendency to minimize the solid-liquid interfacial area. The gelling of inorganic oxide sols is perhaps the most widely known example of this phenomenon (10). However, the arrangement of the primary particles or crystallites in a gel does not in general correspond to a closely packed aggregated state, since the collision processes which lead to aggregation of the primary particles present in the parent sol are influenced by the random thermal (i.e., Brownian) movement of the dispersed crystallites. The rearrangement of the

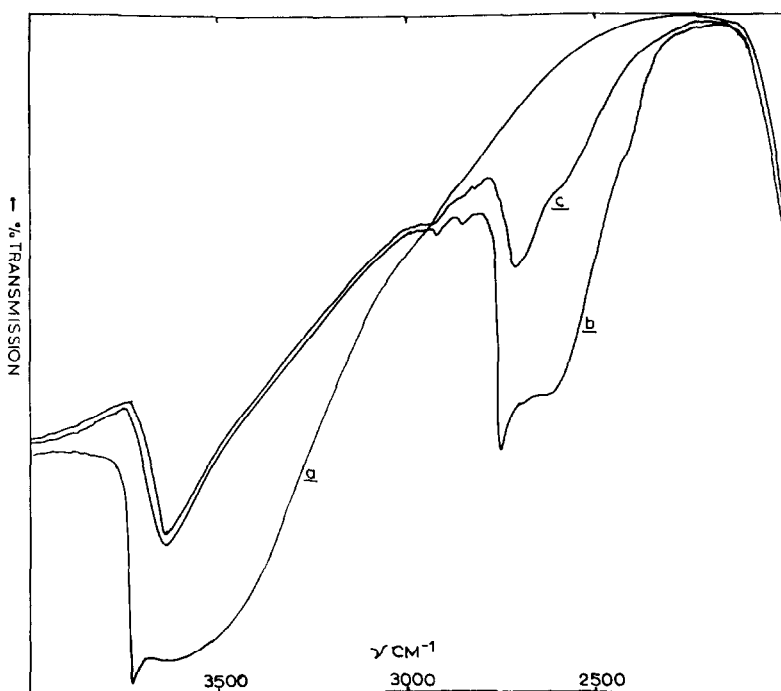


FIG. 3. The infrared spectrum of R.A. 3 powder after evacuation at 25°C at 1×10^{-4} torr (a); after treatment with D_2O vapor at 25°C and subsequent evacuation at 1×10^{-4} torr (b); and after treatment of (b) with boron trichloride vapor at 25°C (c).

primary crystallites in such a non-close-packed or open gel structure to give a more closely packed configuration will be an activated process, the energy of activation

perhaps being closely related to the work required to break the initial intercrystallite adhesions.

The work of Davydov *et al.* (8) clearly shows that this crystallite rearrangement (i.e., hydrothermal treatment) produces an increase only in the 3650-cm^{-1} absorption band of the infrared spectrum of the corresponding rearranged gels. A similar though less pronounced increase was found in the present study when the spectrum of R.A. 3 (Fig. 3) was compared to that of R.A. 2 (Fig. 4). The increased absorption intensity at 3650 cm^{-1} found for the former solid is greater than for the latter and is the result of the more vigorous rehydration conditions employed in its preparation (11). The results of such studies are also in accord with the suggestion that the infrared absorption band at 3650 cm^{-1} corresponds to interparticle (or intercrystallite) hydroxyl interactions.

It is worthwhile noting here that in general, the specific surface area of the solid as measured by adsorption techniques at the gas-solid or solid-liquid interface reflects

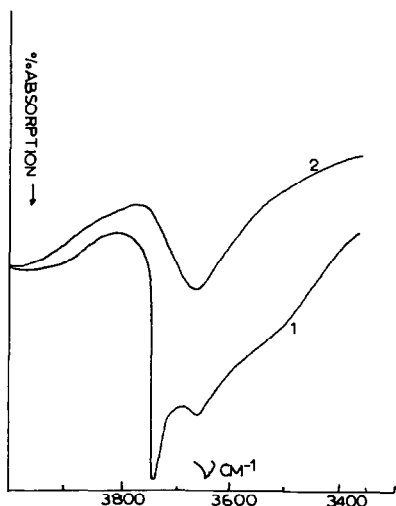


FIG. 4. The infrared spectrum of R.A. 2 powder after evacuation at 25°C at 1×10^{-4} torr (1); and after exchange with D_2O vapor at 25°C followed by evacuation at 1×10^{-4} torr (2).

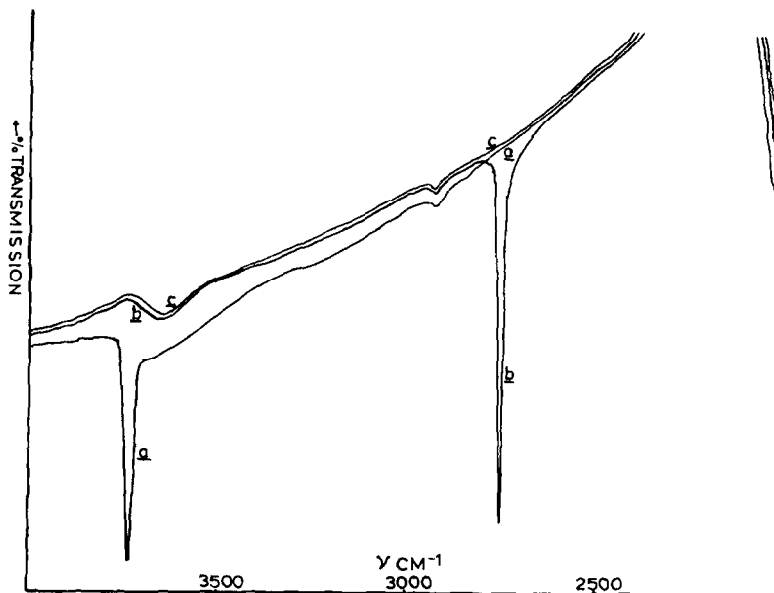


FIG. 5. The infrared spectrum of an R.A. 3/700 powder sample after evacuation at 25°C at 1×10^{-4} torr (a); after exchange with D₂O vapor at 25°C followed by evacuation at 1×10^{-4} torr (b); and after treatment of (b) with boron trichloride vapor (c).

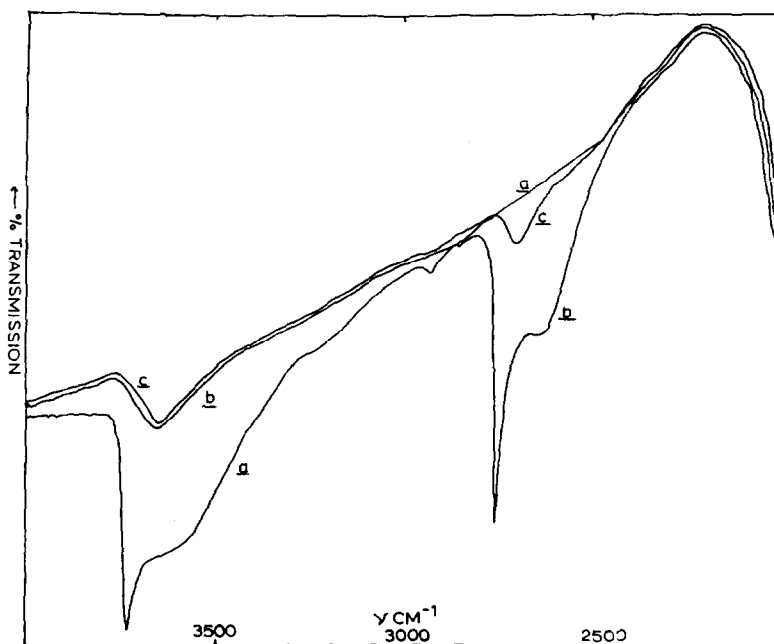


FIG. 6. The infrared spectrum of a rehydrated sample of R.A. 3/700 powder (R.R.A. 3/700) after evacuation at 25°C at 1×10^{-4} torr (a); after treatment with D₂O vapor at 25°C followed by evacuation at 1×10^{-4} torr (b); and after treatment of (b) with boron trichloride vapor at 25°C (c).

only the external area of the larger aggregates. Thus, since thermogravimetric techniques measure the total hydroxyl content of the whole solid phase, as the aggregates become larger their specific surface area becomes smaller and the apparent surface hydroxylation increases above the true value of about 4.6 OH's per 100 Å² as found by de Boer and Vleeskens (14), and more recently by other workers (3, 17) studying silicas in which the hydroxyls within the aggregates had been irreversibly removed by thermal treatment.

4. Thermal Treatment

When silicas and other oxides are heated the intensities of all the absorption bands in the infrared spectrum decrease. There have been numerous detailed studies of these thermal dehydroxylation phenomena (1, 12, 13). In the present context the most significant feature of thermal dehydroxylation is that the species responsible for the absorption band at 3650(2690) cm⁻¹ is irreversibly removed by heating the sample at temperatures above about 500°C. See Fig. (5).

That is to say that, whereas the true surface species responsible for the absorption bands at 3745(2755) cm⁻¹ and 3550(2620) cm⁻¹ may be regenerated by rehydrating the solid in liquid water at room temperature, the species responsible for the 3650(2690) cm⁻¹ absorption band may not be recovered by such means, with the exception of the small number of fresh interparticle junctions formed by the hydrotensile forces produced during rehydration and drying of the ignited powdered solid (see Fig. 6). Ignited discs show virtually zero absorption at 3650(2690) cm⁻¹ when they are similarly rehydrated.

This thermal annealing process (12, 14) is an interesting one in that it corresponds to the replacement of the relatively weak interparticle hydroxyl hydrogen bonds by the stronger silicon-oxygen-silicon system. It follows that if gels are stored or dried under conditions in which this annealing process occurs—even if only slowly, as for example under ambient conditions—then the initial gel structure will be progressively set in such a way that the array becomes progressively

more resistant to hydrothermal rearrangement. Such effects are certainly observed generally for silica gels (15).

It also follows from the above arguments that there should be an inverse relationship between the mechanical strength of cold-pressed oxide powder aggregates and the mean crystallite size. Furthermore the use of hot-pressing techniques with such hydroxylated solids should also lead to an increase in the aggregate's mechanical strength, even at temperatures below those at which viscous flow of the solid phase occurs. Such effects are indeed well known to ceramicists (16).

CONCLUSIONS

Finally, it is pertinent to consider whether the effects described in the present paper are specific to silicas. This would seem unlikely, since it would be irrational to argue that the surface hydroxyls of other inorganic oxides are capable of hydrogen bonding along the surface of the solid but are incapable of interacting across the interparticle junctions in pressed discs or gels. If one takes account of the current wide usage of the pressed-disc technique in studies designed to characterize the surface hydroxylation of inorganic oxide powders and the way in which these results are then used to interpret the data obtained in gas and solution absorption studies which are usually carried out on the powdered solid, then effects such as those described above may be worthy of consideration.

ACKNOWLEDGMENTS

We thank Mr. S. A. Mitchell and Dr. D. Barby of Unilever Limited for helpful discussions during the course of this work.

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