The Surface Hydroxylation of Silica

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The surface hydroxylation of silica gels and powders has been studied by determining the stoichiometry of the reactions of $SiMe_2Cl_2$, $TiCl_4$, and BCl_3 with the surface hydroxyl groups. The results demonstrate that the fully hydroxylated silica surfaces studied carry two distinct types of surface hydroxyl sites, which are distributed as follows: 1.4 ± 0.1 single surface hydroxyls (type A sites), and about 3.2 ± 0.1 interacting hydroxyl groups arranged in pairs (1.6 ± 0.1 type B sites). On heating the silicas above ambient temperatures, *in vacuo*, the type B sites are progressively removed. By correlating this result with earlier studies, it is concluded that at temperatures of $500 \pm 50°$, *in vacuo*, virtually all the type B sites are eliminated. However, the type A site concentration remains constant at evacuation temperatures up to $600 \pm 50°$ at around 1.4 ± 0.1 A sites/100 $Å^2$.

These conclusions suggest that the silica surface corresponds to an array of different crystal planes, some of which contain OH groups at relatively large interhydroxyl spacings and others containing OH groups held in such a way as to promote interhydroxyl hydrogen bonding.

The surfaces of all metal and metalloid oxides are covered to varying degrees by hydroxyl groups or ions which play an important role in the adsorption processes occurring at oxide surfaces. The surface properties of silica are of great theoretical and practical importance and consequently this oxide has been the subject of a great deal of research. The parameters which require definition for a satisfactory description of the surface properties are the concentration, coordination and stereochemistry of the surface hydroxyls. A number of experimental techniques have proved to be of particular value in this respect.

Using thermogravimetric methods, de Boer and Vleeskens[1] found that silicas approached a limiting surface coverage or concentration of 4.6 hydroxyl groups per 100 $Å^2$ of surface ($n_{OH} = 4.6$) after they had been repeatedly rehydroxylated and annealed at 450°. They concluded that the fully annealed and rehydrated surface of silica closely resembled the rhombohedral face of β-tridymite, in which each of 4.6 surface silicon atoms per 100 $Å^2$ of surface carried one hydroxyl group. The hydroxyls in excess of this limiting value were attributed to surface defects and arrangments whereby some of the surface silicon atoms carried more than one hydroxyl. Other workers[2-4] utilizing infrared spectroscopic techniques have since attributed the excess hydroxyl concentration to hydroxyl groups located within the bulk of the solid. Such bulk hydroxyls are removed during thermal treatment and only a very few are regenerated during the rehydroxylation process.[5]

As a result of such studies, it has become apparent that the model of de Boer,[1] *et al.*, for the surface hydroxylation of silica is insufficient to explain the observed results. Its major defect is that it predicts that the limiting surface contains hydroxyl groups in such a way that their oxygen atoms are 5 Å apart,

hence implying that interhydroxyl hydrogen-bonding interactions cannot occur due to this relatively large distance. It has been clearly demonstrated that a substantial fraction of the hydroxyl groups of both freshly prepared and hydroxylated annealed silicas undergo hydrogen-bonding interactions.[2-4]

In a recent publication, Peri and Hensley[6] have produced a different model for the silica surface. These workers have used computer techniques to simulate *via* "Monte Carlo" statistical methods, crystallographically viable surface hydroxylation patterns. In their paper, Peri and Hensley[6] produce two possible models for the surface hydroxylation. One (see Figure 3, ref 6) corresponds to a randomly hydroxylated 0001 face of β-tridymite, which contains approximately 1.5 single or non-hydrogen-bonded hydroxyls per 100 $Å^2$ of surface and about 3-3.5 hydrogen-bonded hydroxyls per 100 $Å^2$ of surface. However, Figure 3 in Peri and Hensley's paper[6] shows no differentiation between first (*i.e.*, surface) and second-layer silicon atoms. This cannot therefore be a correct model for the silica surface and any discussion based on it is likewise invalid. The other model (see Figure 4 of ref 6) corresponds to a surface resembling an idealized 100 face of β-cristobalite. When this model is fully hydroxylated each silicon atom carries two hydroxyl groups giving a total concentration of 7.9 hydroxyls per 100 $Å^2$ of surface.

(1) J. H. de Boer, M. E. A. Hermans, and J. M. Vleeskens, *Proc. Koninkl. Ned. Akad. Wetenschap.*, B, **60**, 44 (1957).

(2) F. H. Hambleton, J. A. Hockey, and J. A. G. Taylor, *Trans. Faraday Soc.*, **62**, 801 (1966).

(3) J. J. Fripiat and U. Uytterhoeven, *J. Phys. Chem.*, **66**, 800 (1962).

(4) V. Ya. Davydov, U. V. Kiselev, and L. T. Zhuravlev, *Trans. Faraday Soc.*, **60**, 2254 (1964).

(5) F. H. Hambleton, J. A. Hockey, and A. J. Tyler, *J. Catal.*, **13**, 35 (1969).

(6) J. B. Peri and A. L. Hensley, Jr., *J. Phys. Chem.*, **72**, 2926 (1968).

Experimentally the surface concentrations of single (A site) and paired (B site) hydroxyls may be assessed by considering the stoichiometry of the chemical reaction of the surface hydroxyls with hydrogen-sequestering reagents. As a result of their own studies using $AlCl_3$ and $SiCl_4$, Peri and Hensley[6] have chosen the 100 β-cristobalite model, since they state that their experimental results show that all the hydroxyls react in pairs even after evacuation of some of the solids at temperatures in excess of 600°.

The object of the present paper is to show that there exists a significant body of experimental evidence in favor of a silica surface containing both A and B sites and also to postulate a theoretical model in accord with these observations.

## Experimental Section and Results

The results of the infrared, thermogravimetric and adsorption studies referred to in this paper have been published elsewhere[7-10] and the reader is thus referred to this literature as required. The only experimental data reported here is that which concerns the chemical reactions of $TiCl_4$, BCl_3 and $SiMe_2Cl_2$ with the surface hydroxyls of a range of silica gels and powders. All the experimental techniques have one common important feature. All the reactions were investigated by chemical analysis of the solid phase for residual chlorine, thereby circumventing any possible artifactual results produced by the reactions of the halogen compounds with any vacuum stopcocks, greased or otherwise. In our experience, BCl_3, $TiCl_4$ and halogenosilanes react with the organic polymer diaphragms of greaseless stopcocks and vacuum greases to produce gaseous HCl in significant quantities.

It is also important to recognize that if the surface hydroxyls of a silica, which also contains bulk hydroxyls, are reacted with halogen compounds at low temperatures ($\leq 200°$) then the bulk hydroxyls remain unaffected. If the unreacted solid is then heated to 600°, the bulk hydroxyls condense, releasing water from the interior of the particles. This water hydrolyzes the halogen containing surface products thereby producing HCl in the gas phase. All freshly prepared silicas in our experience contain an appreciable quantity of such bulk hydroxyls often equivalent to an n_{OH} value of 1–2 per 100 Å².

The following experiment is reported as an illustration of this point. A silica containing "bulk hydroxyls"[5,8,10] (i.e., hydroxyls unavailable for reaction with molecules such as D_2O, BCl_3, $AlCl_3$, $SiMe_xCl_{(4-x)}$) was mounted in a cell[11] and its spectrum recorded after evacuation at 2×10^{-4} Torr at room temperature. The spectrum obtained is shown in Figure 1a and is similar to that obtained by Davydov and his coworkers[4] for similar internally hydroxylated silicas. Reaction with BCl_3 at room temperature leaves a broad residual OH absorption band corresponding to the internal

hydroxyls as defined by this reagent. The excess BCl_3 vapor and the HCl produced in the reaction were then evacuated at room temperature as before and the corresponding spectrum recorded (Figure 1b). The cell was then closed from the pumps and the sample heated in situ for 90 min at 300°. The spectrum (Figure 1c) was then recorded once more without evacuating the cell. This spectrum illustrates that this procedure leads to the production of a surface containing SiOH and BOH species of the type described previously[7] and also to the production of gaseous HCl as evidenced by the finely resolved absorption pattern observed around 2890 cm^{-1}.

Another suggested explanation[12] of the spectra shown in Figure 1 is that the residual absorption band at 3650 cm^{-1} (1b) corresponds to interacting surface hydroxyls that cannot react completely as pairs with BCl_3 at ambient temperatures owing to steric hindrance—a possibility suggested by Peri and Hensley[6]—but can react to completion on subsequent heating to 300°

(a)   (b)

(c)
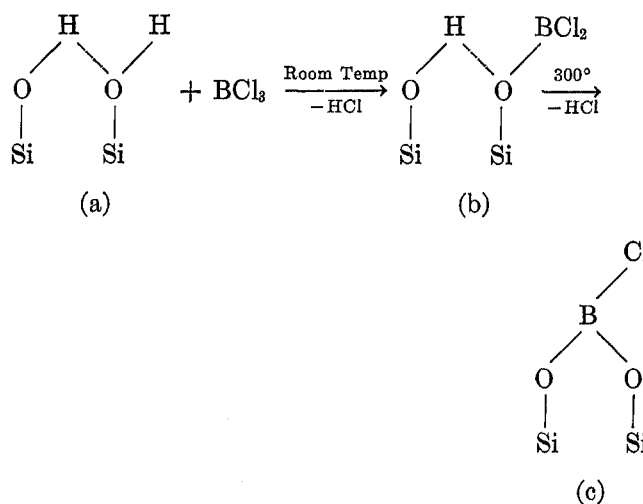
However, the second reaction at 300° on this scheme, although producing HCl in the gas phase as observed (Figure 1c), would not produce the observed hydroxylated species SiOH and BOH (Figure 1c). Noting the results of our other studies on the BCl_3, SiO_2, $H_2O–D_2O$ system[2,5,7] and spectrum c, we conclude that the hydrolyzing reagent produced on heating the room temperature reacted species (Figure 1b) must be HOH and

(7) F. H. Hambleton and J. A. Hockey, *Trans. Faraday Soc.*, **62**, 1694 (1966).

(8) C. G. Armistead and J. A. Hockey, *ibid.*, **63**, 2549 (1967).

(9) J. A. G. Taylor and J. A. Hockey, *J. Phys. Chem.*, **70**, 2169 (1966).

(10) A. J. Tyler, Ph. D. Thesis, Manchester University, Manchester, England, 1968.

(11) C. G. Armistead, F. H. Hambleton, J. A. Hockey, and J. W. Stockton, *J. Sci. Instrum.*, **44**, 872 (1967).

(12) We thank one of the referees for bringing this possibility to our notice. However, as is now indicated in the text, we do not believe it to be a viable explanation of the experimental results summarized by the spectra in Figure 1.

Table I

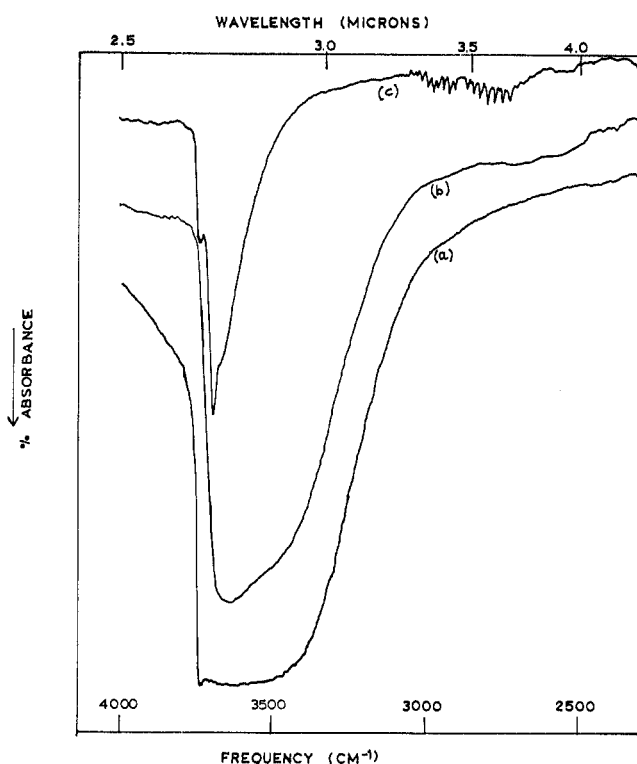| Sample	Reagent	Site concn/100Å²	
		Type A	Type B
R. A. 3	TiCl$_4$	1.4 ± 0.1	3.2 ± 0.1
R. R. A. 3/700	TiCl$_4$	1.4 ± 0.1	3.2 ± 0.1
R. A. 3/700	TiCl$_4$	1.3 ± 0.1	...
R. A. 3	SiMe$_2$Cl$_2$	1.3 ± 0.1	...[a]
R. R. A. 3/700	SiMe$_2$Cl$_2$	1.3 ± 0.1	...[a]
R. A. 3/700	SiMe$_2$Cl$_2$	1.2 ± 0.1	...[a]

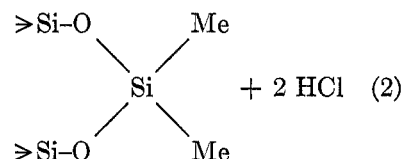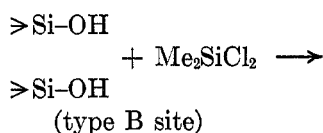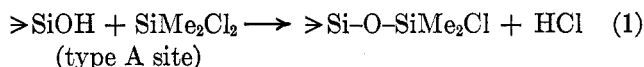[a] Indeterminable with SiMe$_2$Cl.

Figure 1. Spectrum of silica holding both surface and "bulk" hydroxyls (a) before reaction with BCl$_3$, (b) after reaction with BCl$_3$ followed by evacuation at room temperature, and (c) after subsequent heating for 90 min at 300° without evacuation.

not OH. Hence we do not feel that this "steric hindrance" viewpoint is tenable.

Thus an experimental procedure of this type, which corresponds closely to that of Peri and his coworkers,[6] leads to the production of HCl in excess of that obtained from the reaction of BCl$_3$ and the surface hydroxyls. Similar results are obtained with other multichlorinated hydrogen-sequestering agents. Thus, if the stoichiometry of the reactions of such reagents with the silica surface hydroxyls are determined by measuring the HCl produced in an experiment of the type described above, a false picture of the reaction is obtained. One would conclude from such results that more of the surface hydroxyls were "paired" than was actually the case.

In Table I, the silicas that we have studied are listed, together with the results obtained for their surface hydroxylation in terms of the analyses carried out as described below.

SiMe$_2$Cl$_2$. (For full experimental details see ref 8.) The silica R. A. 3 was evacuated to constant weight at 300° followed by reaction with SiMe$_2$Cl$_2$ vapor to constant weight and final evacuation at 300° and 1 × 10^{-4} Torr. The solid reaction product contained chlorine equivalent to 1.3 ± 0.1 chlorine atoms per 100 A² of surface. Considering the reactions of SiMe$_2$Cl$_2$ with type A and type B sites, we have

$$\ge SiOH + SiMe_2Cl_2 \longrightarrow \ge Si\text{-}O\text{-}SiMe_2Cl + HCl \quad (1)$$
(type A site)

$$\ge Si\text{-}OH$$
$$\qquad\qquad + Me_2SiCl_2 \longrightarrow$$
$$\ge Si\text{-}OH$$
(type B site)

$$\ge Si\text{-}O \diagdown \qquad \diagup Me$$
$$\qquad\qquad Si \qquad + 2 HCl \quad (2)$$
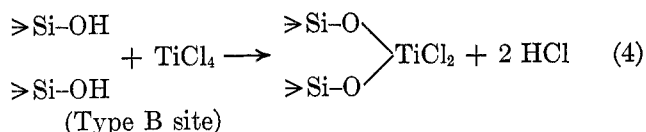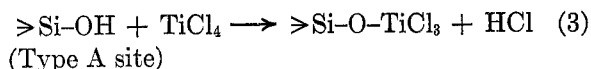$$\ge Si\text{-}O \diagup \qquad \diagdown Me$$

It can be seen from this reaction scheme that only Type A sites can lead to residual chlorine in the reaction products. Furthermore, the number of type A sites is equal to the number of residual chlorine atoms, that is 1.3 ± 0.1 type A sites/100 A². Reaction of an R. A. 3 silica, that had been evacuated to constant weight at 500°, with SiMe$_2$Cl$_2$ at 300° again gives a type A site concentration of 1.3 ± 0.1 per 100 A² of surface.

On the basis of the model chosen and discussed by Peri and Hensley[6] only reaction 2 should occur, which would result in there being no residual chlorine on the silica surface after treatment with SiMe$_2$Cl$_2$.

TiCl$_4$. Infrared spectroscopic studies[13] have shown that TiCl$_4$ reacts with all the 4.6 hydroxyl groups present on the surface of a fully hydroxylated annealed

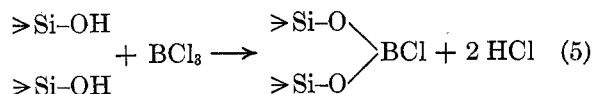(13) J. Murray and J. A. Hockey, unpublished results.

Aerosil (R. R. A. 3/700).[5] The silicas were evacuated at 2×10^{-5} Torr at room temperature to constant weight on a MacBain balance. The weight change, produced by the reaction of the sample with TiCl$_4$ vapor *in situ* was measured directly, after complete removal by evacuation of the excess reagent. The observed weight changes are in accord with the reactions 3 and 4 shown below occurring in almost equal preponderance.

$$\text{>Si-OH} + \text{TiCl}_4 \longrightarrow \text{>Si-O-TiCl}_3 + \text{HCl} \quad (3)$$
(Type A site)

$$\begin{matrix} \text{>Si-OH} \\ \\ \text{>Si-OH} \end{matrix} + \text{TiCl}_4 \longrightarrow \begin{matrix} \text{>Si-O} \\ \\ \text{>Si-O} \end{matrix} \Big\rangle \text{TiCl}_2 + 2\,\text{HCl} \quad (4)$$
(Type B site)

For a silica with a B. E. T. surface area of 150 m^2/g carrying 4.6 OH/100 Å^2 of surface, the weight increase per gram of silica on reaction with TiCl$_4$, assuming that there are 1.4 OH/100 Å^2 reacting as in eq 3 and 3.2 hydroxyl groups reacting as 1.6 type B sites, as in eq 4, is equal to 101 mg per gram of solid.

For the same silica reacting as in eq 4 only, as it would were Peri and Hensley's model correct, 2.3 hydroxyl pairs or type B sites/100 Å^2 would react. This would produce a weight change of 67 mg per gram of solid. The observed weight changes were always within 1–2% of the first figure of 101 mg per gram of solid.

BCl$_3$. Two grams of silica was dried to constant weight at 180° *in vacuo* and exposed to BCl$_3$ vapor at room temperature. Under such conditions, all the surface hydroxyls react, as was confirmed by infrared spectroscopic techniques.[5] After prolonged evacuation of the HCl and excess BCl$_3$ at 100°, the chlorine content of the reacted solid was determined by dissolving it in 1 *M* sodium hydroxide solution and titrating this solution for chloride potentiometrically. This process was repeated for another sample of the same silica after it had been evacuated to constant weight at 450°. The analyses were duplicated and agreement of 3% or better was obtained in all cases. Taking the chloride analyses in Table II for the 450° evacuated samples and assuming that the surface contains only type B sites as postulated by Peri and Hensley,[6] we have the following reaction

$$\begin{matrix} \text{>Si-OH} \\ \\ \text{>Si-OH} \end{matrix} + \text{BCl}_3 \longrightarrow \begin{matrix} \text{>Si-O} \\ \\ \text{>Si-O} \end{matrix} \Big\rangle \text{BCl} + 2\,\text{HCl} \quad (5)$$

We note that each chlorine atom in the solid reaction product is equal to two surface hydroxyls. On this basis, after evacuation at 450°, all the silicas studied carry between 4.4–6.6 surface hydroxyls per 100 Å^2. However, independent thermogravimetric analyses of the same samples show that the total hydroxylation including any bulk hydroxyls still present is less than

3 hydroxyl groups/100 Å^2 of surface. Similarly, using reaction 5 to analyze the data obtained at 180° yields n_{OH} values between 7.4 and 9.2. Thermogravimetric analysis again shows the total n_{OH} value, including any bulk hydroxyls present, to be always less than 6 for each of the samples. Consequently we conclude that analysis of the data on the basis of eq 5 alone cannot be correct. Calculations consistent with the observed chlorine contents can only be obtained if we include another reaction (6)

$$\text{>Si-OH} + \text{BCl}_3 \longrightarrow \text{>Si-O-BCl}_2 + \text{HCl} \quad (6)$$
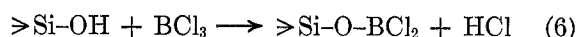
which would produce two chlorine atoms for each hydroxyl group. By assuming that all the interacting hydroxyls on type B sites have been removed by prolonged evacuation at 450°, the only reaction which could occur on these silicas is that presented in eq 6 above. Analyzing the data in Table II for the 450° sample in this way produces a surface hydroxyl concentration of 1.4 ± 0.1 hydroxyl groups per 100 Å^2. (This value may be a little high due to the incomplete removal of all the type B sites at 450°.) By subtracting from the total chlorine content of the 180° sample the contribution due to these 1.4 single surface hydroxyls we obtain the chlorine content due to reactions occurring at the paired type B hydroxyl sites. The total hydroxyl contents are below the limiting room temperature value of 4.6/100 Å^2 due to the fact that at 180° a number of the type B sites have already been removed.

There are other data in the literature supporting this picture of approximately equal numbers of type A and type B sites per 100 Å^2 on a fully hydroxylated surface. Boehm, *et al.*,[14] show that the Cl:B ratio of the solid product varies with the prior outgassing temperature of the silica, gradually increasing with temperature to a value of 2:1 after prior evacuation at 450°. Clearly this increasing ratio is only consistent with an increasing predomination of reaction 6 as the silica surface is dehydroxylated progressively by removal of the type B sites.

Fripiat[15] and his coworkers have studied the reaction of diborane with the surface hydroxyls of silica. They analyzed the surface reactions by studying the ratio of the hydrogen evolved to the diborane consumed on reacting hydroxylated silicas with the diborane—they called this ratio the "primary hydrolysis ratio." They also measured the hydrogen evolved when the evacuated solid reaction product was hydrolyzed by water vapor; this ratio they called the "secondary hydrolysis ratio." This secondary ratio corresponds to the volume of hydrogen produced on treatment with water vapor to the volume of diborane initially consumed.

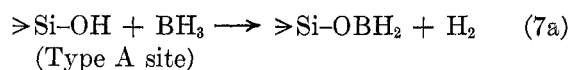Fripiat, *et al.*,[15] also showed that the diborane dis-

(14) H. P. Boehm, M. Schneider, and F. Arendt, *Z. Anorg. Allg. Chem.*, **320**, 43 (1966).

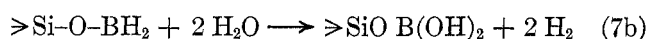(15) J. J. Fripiat and M. Van Tongelen, *J. Catal.*, **5**, 158 (1966).

Table II

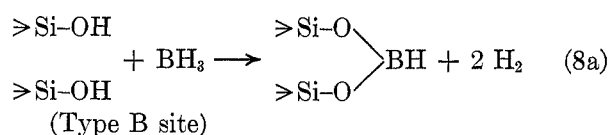| Sample | Sample heated at 450° *in vacuo* | | Sample heated at 180° *in vacuo* | | | |
	Cl/100 Å²	OH gps/100 Å²	Cl/100 Å²	Difference between 180 and 450°	No. of type B sites	Total OH/100 Å²
Aerosil	2.8	1.40	3.9	1.1	1.1	3.6
Aerosil (rehydrated)	3.0	1.50	4.4	1.4	1.4	4.3
T. K. 800	3.2	1.60	4.6	1.4	1.4	4.4
Manosil VN3	3.0	1.50	4.4	1.4	1.4	4.3

sociated to two molecules of BH_3 prior to reaction with the surface hydroxyls. The reactions involved at type A and type B sites may thus be written
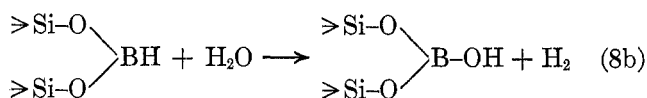
$$\gt Si-OH + BH_3 \longrightarrow \gt Si-OBH_2 + H_2 \quad (7a)$$
(Type A site)

Primary hydrolysis ratio = 2 (*i.e.*, 2 H_2/B_2H_6)

$$\gt Si-O-BH_2 + 2 H_2O \longrightarrow \gt SiO\ B(OH)_2 + 2 H_2 \quad (7b)$$

Secondary hydrolysis ratio = 4 (*i.e.*, 4 H_2/B_2H_6)

$$\begin{matrix} \gt Si-OH \\ \quad\quad\quad + BH_3 \longrightarrow \\ \gt Si-OH \end{matrix} \begin{matrix} \gt Si-O \\ \quad\quad >BH + 2 H_2 \\ \gt Si-O \end{matrix} \quad (8a)$$
(Type B site)

Primary hydrolysis ratio = 4 (*i.e.*, 4 H_2/B_2H_6)

$$\begin{matrix} \gt Si-O \\ \quad\quad >BH + H_2O \longrightarrow \\ \gt Si-O \end{matrix} \begin{matrix} \gt Si-O \\ \quad\quad >B-OH + H_2 \\ \gt Si-O \end{matrix} \quad (8b)$$

Secondary hydrolysis ratio = 2 (*i.e.*, 2 H_2/B_2H_6)

Their results show that the primary and secondary hydrolysis ratios vary with prior evacuation temperature. The former quantity decreases from a value close to 3 and 2 as prior evacuation temperature is increased from ambient to 400°, while the secondary hydrolysis ratio increases from 3 to 4.

It can be seen from reactions 7a and 8a that an approximately equal preponderance of type A and type B sites would give a primary hydrolysis ratio of 3 and that the gradual removal of the type B sites would result in this value decreasing to 2. A similar explanation can be accorded to the increase in the secondary hydrolysis ratio from 3 to 4 over the same range. Unfortunately, silicas heated to higher temperatures such that the n_{OH} value decreases to $\leq 1.4/100$ Å² react so slowly with diborane that the method apparently becomes invalid as a means of measuring surface hydroxyl concentrations.[15]

Discussion

In considering the results presented above and previous workers' interpretations of this system one recognizes that they have tried to find one crystal plane which, existing as a hydroxylated surface, carries the

correct number of hydroxyls. However, as recent work has shown,[5] silicas consist of primary crystallites of the order of 10's of Å in "diameter" aggregated into larger clumps of the order of 100's of Å in "diameter." Now crystals or crystallites of high symmetry (*e.g.*, a cubic (rock salt) structure as in MgO) will exhibit surfaces that are identical in their anion–cation arrays. However, crystallites of lower symmetry such as in β-tridymite or β-cristobalite cannot exhibit identical surface planes over all their exterior surfaces. Thus the search by de Boer, *et al.*,[1] Hockey and Pethica,[16] and more recently by Peri and Hensley[6] for "the" crystal plane which existing *in extenso* explains the observed hydroxylation of silicas is essentially wrong in emphasis. If one assumes a number of crystal planes to exist in the surface of silicas the difficulties of interpretation disappear.

As an example, let us consider the likely dehydroxylation behavior and structure of two crystal planes which occur in both β-tridymite and β-cristobalite. Both have been discussed in the present context by previous workers.[1,6]

One is the 0001-β-tridymite face discussed by Peri and Hensley[6] (its equivalent in β-cristobalite is the octahedral face discussed by de Boer[1]). We note here for convenience that the β-cristobalite and β-tridymite polymorphs of silica have virtually identical densities and differ in their crystal lattices only as a result of the different relative dispositions of their first and third layer oxygen atoms as previously described.[1,16]

The other corresponds to the 100 β-cristobalite face (again β-tridymite as Peri and Hensley[6] point out can also exhibit a similar low-index surface plane).

The former (0001 β-tridymite) contains 4.6 surface silicon atoms spaced 5.0 ± 0.1 Å from their equidistant nearest neighbors. The terminal Si–O bonds (*i.e.*, the Si–O bonds of the surface hydroxyls) are orthogonal to the surface plane and hence there is no possibility of such surface groups undergoing mutual hydrogen bonding or of interacting chemically in such a way as to eliminate water readily and easily. The arrangement presented by the 100 β-cristobalite type of face, however, is one in which the surface silicon atoms are in

(16) J. A. Hockey and B. A. Pethica, *Trans. Faraday Soc.*, **57**, 2247 (1961).

rows (see Figure 4 of ref 6) with each silicon atom carrying two hydroxyl groups. Equally important is the fact that the terminal Si–O(OH) bond axis is at a low angle to the surface plane [(180 − 109° 28')/2 $\simeq$ 35°] and point in such a way that the oxygen atoms of the hydroxyl groups on adjacent surface silicon atoms are held close together. Such an arrangement would produce paired hydrogen-bonded hydroxyls.

Dehydroxylation of such a surface, by the elimination of one molecule of water per pair of interacting hydroxyls would be relatively easy and proceed in such a manner as to leave only paired hydroxyls remaining on the surface and a corresponding number of strained siloxane links.

Proceeding now to consider the extent of the hydroxylation of each of these crystal planes, we note that the single hydroxyl concentration as measured by both chemical and infrared spectroscopic techniques remains constant at ignition temperatures up to 600 ± 50°. We therefore conclude that those parts of the equilibrium room-temperature silica surface which corresponds to the 0001 β-tridymite (or equivalent) crystal plane are fully hydroxylated between 0 and 600°. Thus, out of the total surface area of the solid approximately 1.4/4.6, i.e., ~30% of the surface corresponds to the 0001 face of β-tridymite or its equivalent face in β-cristobalite.

Were it fully hydroxylated, a surface corresponding to the 100 plane of β-cristobalite would contain 7.9 hydroxyl groups per 100 Å^2. Therefore, by analogous arguments to those presented above we may conclude that those parts of the equilibrium room-temperature surface which correspond to the 100 β-cristobalite or equivalent crystal plane are hydroxylated to only about 60% of their maximum possible hydroxylation. That is to say that 70% of the equilibrium room-temperature silica surface corresponds to a partially dehydroxylated 100 plane of β-cristobalite (or its equivalent face in β-tridymite) giving a concentration of 3.2 interacting hydroxyls (or 1.6 type B sites) per 100 Å^2 of *total* surface area.

With the exception of Peri and Hensley,[6] previous workers in this field[1,16] have assumed that fully hydroxylated surfaces (i.e., after evacuation at 25°) are indeed fully hydroxylated. Perhaps a more realistic view can be achieved if one considers that the concentration of interacting surface hydroxyls decreases steadily as the sample is heated from room temperature upwards. In view of this there seems little a priori evidence that significant dehydroxylation has not occurred on ignition in vacuo at 25°. That is to say that if dehydroxylation has proceeded to a certain extent at say 450°K, then one should not assume that a similar, though less extensive, depopulation has not occurred at 300°K.

The presence after room temperature evacuation of strained siloxane links would imply that adsorbing water onto a nonmicroporous room-temperature evacuated silica would result in the creation of interacting paired hydroxyls and also to a spatial relaxation of the silica lattice. In the case of the production of interacting hydroxyls at strained siloxane links it should be noted that Anderson and Wickersheim[17] have shown that the adsorption of water onto silicas at room temperature led to an increase in the intensity of the infrared absorption band at 3550 cm^{-1}. In the case of the spatial relaxation of the silica lattice during this rehydration process, Folman and Yates[18] have noted that adsorbing water onto silicas evacuated at room temperature results in an expansion of the sample.

Conclusions

The results presented in this paper suggest that at ambient temperatures the surface hydroxylation of "fully" hydroxylated silicas corresponds to a surface containing about 4.6 hydroxyl groups per 100 Å^2 of total surface area. Of these about 1.4 ± 0.1 groups exist as single non-hydrogen-bonded species (1.4 A type sites/100 Å^2). The remaining 3.2 hydroxyls exist as pairs (1.6 ± 0.1 B type sites/100 Å^2).

Dehydroxylation of such a surface results in the complete removal of type B sites at temperatures of 500 ± 50°. At this stage of dehydroxylation the surface contains only 1.4 isolated or single hydroxyls/100 Å^2 of surface.

Referring to infrared spectroscopic data published elsewhere[5] this model is in accordance with the assignment of the "high" frequency (3750 cm^{-1}) absorption band to the single hydroxyl species and the assignment of the 3550 cm^{-1} absorption band to the hydrogen-bonded surface species. As shown in ref 5, the nonexchangeable band centered at 3650 cm^{-1} observed in freshly prepared silicas corresponds to hydrogen-bonded internal or bulk hydroxyls.

It is noticeable that the mysterious[15] value of n_{OH} = 1.4 ± 0.1 discussed by a number of workers in recent years,[6,8,15,19–21] is equal to the single surface hydroxyl concentration/100 Å^2. The persistent value of 1.4 ± 0.1 single groups obtained up to temperatures of at least 600° indicates their temperature stability, whereas the progressive removal of the B sites by steadily increasing outgassing temperatures implies a sterically controlled dehydroxylation process of the type described previously.[2]

Finally, lest the purpose of this paper be in part

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misconstrued, it is not intended that it should detract in any way from the undoubted usefulness of the "Monte Carlo" method as originally applied by Peri. This technique would seem to us to be one of the ways in which future experimental determination of the surface hydroxylation of oxide surfaces may be correlated with realistic theoretical models.

The Density Function for End-to-End Lengths of

Self-Avoiding Random Walks on a Lattice

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Accurate coordinate density functions are calculated for the end-to-end separations of short self-avoiding random walks on the tetrahedral and face-centered cubic lattices. The results are extrapolated to describe long walks by assuming an approach to spherical symmetry with increase in number of steps. The form of the density functions so obtained can be represented by an equation used by Domb to describe his exact enumeration data on the cubic lattice. It is suggested that the essential form of the density function is independent of the lattice for long walks.

Introduction

The number and configurational properties of self-avoiding random walks is of importance in the theory of polymer molecules,[2] percolation problems[3] and the susceptibility expansion of the Ising model.[4] There is overwhelming evidence from exact enumeration results[5] and Monte Carlo calculations[6] that the mean square end-to-end length, $\langle r_n^2 \rangle$, of an n-step self-avoiding walk on a lattice has the functional form

$$\langle r_n^2 \rangle = A n^\gamma \tag{1}$$

where $1.18 < \gamma < 1.22$ for walks in three dimensions. There is strong evidence from exact enumeration studies that γ is exactly $^6/_5$, a conclusion also derived theoretically by Edwards,[7] using a self-consistent field approach for a continuum model. Reiss[8] has recently criticized Edwards' approach to the problem and, using a variation principle, has obtained a value of $\gamma = ^4/_3$ in a continuum. It has since been shown, however, that Reiss' solution of the resulting self-consistent field equation was not sufficiently accurate.[9]

Until recently, relatively little work had been carried out on the probability density function of end-to-end separations of self-avoiding walks. Domb[10] and coworkers have fitted exact enumeration data on the cubic lattice to a distribution of the form

$$F(x) = A \exp\left\{-(x/\sigma)^\nu\right\} \tag{2}$$

In this expression, $F(x)$ is the density function of the x coordinate of the end point of the walk, with $\nu = 2.5$ for three-dimensional systems. The arguments of Fisher[11] are in agreement with this result, and Reiss[8] also predicts a non-Gaussian distribution, although Edwards[7] approach suggests that the distribution over r is a *displaced* Gaussian.

It is the purpose of this paper to calculate $F(x)$ exactly for short walks on the tetrahedral and face-centered cubic lattices and to use a procedure for longer walks that assumes an approach of the radial distribu-

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