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Reactive Silica

V.* Sorption of H_2, O_2, CO, and Reaction Mechanisms

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The reactions of simple gases with reactive silica surfaces (prepared by high-temperature degassing of methoxylated Aerosil) were studied using mainly infrared spectroscopic and quantitative gas adsorption measurements. The extensive data point to the existence of a small number of centers of unusual configuration which are responsible for the unusual activity of the adsorbent. The centers are thought to be geminal and to consist of a pair of closely spaced paramagnetic silicon atoms linked by anomalously active oxygen atoms which probably form a peroxo bridge linking the silicons. The reactions of each gas and the reaction mechanisms are considered in detail.

INTRODUCTION

It was reported earlier that the methoxylation, pyrolysis, and subsequent high-temperature degassing of high-surface-area silica caused the adsorbent to be remarkably active in comparison to ordinary silica (*1-3*). The unusual adsorbent produced by the three-step activation process, termed reactive silica (RS), could be produced in a boria-containing form (*4*) and also through the reaction of silica with some silanes (*5*). In order to obtain more information about the properties of RS, which are unlike those of other silicas, and about the special reaction centers responsible for its activity, we have studied the sorption of H_2, O_2, and CO using infrared spectroscopic and gas volumetric techniques.

EXPERIMENTAL METHODS

Most experimental details have been described elsewhere (*1-5*). Quantitative gas adsorption measurements were made with a BET-like vacuum system (*6*) having a very small dead-space and a 25-ml buret. All measurements were carried out at 25°C by measuring the number of molecules present in the gas phase before and after a chemisorption reaction. Gas volumes were always obtained by averaging four buret readings. Infrared spectra were recorded with Beckman IR-7 and IR-12 spectrophotometers in Turin or with a Perkin-Elmer Model 621 spectrophotometer in New York. CO (99.999% purity, from SIO-Milan) was passed through a liquid nitrogen-cooled trap before use.

RESULTS AND DISCUSSION

H_2 *Chemisorption on RS*

Earlier infrared studies have shown that H_2 was chemisorbed by RS in two stages. Exposure of RS to H_2 in the 25-550°C range resulted in the formation of a band at 2226 cm^{-1} attributed to $\equiv$SiH species. That species was unstable above about 550°C;

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* Part IV: Ref. (*5*).

TABLE 1

H_2 Chemisorption on RS[a]

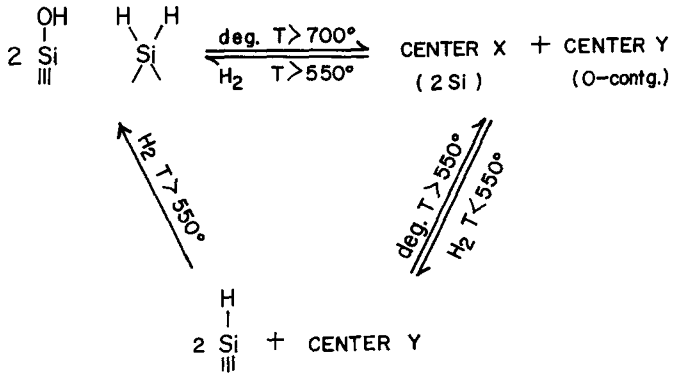
Sample no.	Molecules H_2 adsorbed/g, $\times 10^{-19}$ 1	2	3	4	5	6
A H_2, 350°C	2.94	1.82	1.89	2.96	2.23	4.07
B H_2, 700°C	5.62	3.92	3.58	5.32	5.48	7.53

[a] A: H_2 chemisorbed on RS at 350°C; forms only $\equiv$SiH groups; B: total amount of H_2 chemisorbed by RS on heating first at 350°C as for row A and then at 700°C; forms $=SiH_2$ and $\equiv$Si—OH.

exposure to H_2 at higher temperatures led to increases of a band at 2300 cm^{-1} attributed to $=SiH_2$ species and of the 3750-cm^{-1} $\equiv$Si—OH band. Quantitative relations between the $\equiv$SiH, $=SiH_2$, and $\equiv$Si—OH bands and other considerations led to the suggestion that the remarkable activity of RS was brought about by a reaction site consisting of a silicon radical coupled with a strained siloxane bridge, and a reaction mechanism was postulated.

The previous experiments on H_2 chemisorption have now been repeated and the relationships between the $\equiv$SiH, $=SiH_2$, and $\equiv$Si—OH bands have been confirmed. Also, the amounts of H_2 chemisorbed have been measured and are summarized in Table 1. In order to have the reactions occur at convenient rates, the low-temperature H_2 chemisorption was carried out at 350°C; upon increasing the temperature to 700°C, the $\equiv$Si—H groups were destroyed and $=SiH_2$ and $\equiv$Si—OH groups were formed.

The ratios of rows A and B of Table 1 are close to ½. There is more scatter in these data than in data of Tables 2–5, probably because at high temperatures the contamination problems were more severe and there were uncontrolled side reactions. However, despite the scatter, the ratio between the amounts of H_2 chemisorbed at low and at high temperatures is reasonably close to unity. That ratio definitely rules out the earlier mechanism (*3*), according to which the ratio should be 1/2 and not 1/1. However, the earlier band assignments and spectral relations hold. It is therefore necessary to consider the infrared and quantitative gas adsorption data in terms of some other mechanism such as the following one, which summarizes the data. The data of Table 1 and the relations between infrared bands (*3*) require the factors of 2 shown for some species. Two "centers" are shown in Scheme I. In view of the earlier ESR results, center X is taken to contain silicon radical(s) in some suitable surface environment. The second center Y is included to account for the high-temperature H_2 chemisorption. It is possible to postulate a variety of mechanisms involving the conversion of $\equiv$SiH to $=SiH_2$ groups. However, it is clear that



I

none of them may include any involvement of a siloxane bridge because ordinary silica does not chemisorb H_2. It is consequently necessary to postulate some suitable oxygen-containing group, not consisting of normal siloxane bridges, which is able to supply the oxygen needed for the formation of silanols.

O_2 *Chemisorption on RS*

RS chemisorbed O_2 at room temperature, the reaction being complete within a few seconds. There were no changes in the infrared spectrum of the adsorbent when oxygen chemisorption occurred (Fig. 1). However, exploratory electron spin resonance measurements showed that the paramagnetic species originally present on the adsorbent (*2*, *3*) were altered by the O_2 chemisorption (*7*). The chemisorption of O_2 on the silica network of siliceous materials containing paramagnetic centers has already been observed in some instances to lead to oxygen paramagnetic species (*8–11*). These might be $\equiv$Si—O$^\bullet$ or $\equiv$Si—O—O$^\bullet$ groups, but the latter seems to be formed. In particular, Schrader, Wissing, and Kubsch (*9*), who produced surface paramagnetic centers by grinding crystalline quartz, demonstrated that oxidation and reduction effects as well as the thermal generation of oxygen pointed to the existence of peroxo radicals on their material.

As pointed out earlier and indicated in Scheme I, the low-temperature H_2 chemisorption was reversible. RS was exposed to H_2 at 350°C; the amounts taken up are shown in row A of Table 2. The samples were degassed at 550–600°C to restore them to their initial state, and were then exposed to O_2 at 25°C. The amounts of O_2 taken up are shown in row B of Table 2. Note that the H_2 chemisorption was dissociative and involved center X. O_2 chemisorption modified center X and therefore also in-

TABLE 2
O_2 CHEMISORPTION ON RS[a]

Sample	Molecules adsorbed/g, $\times 10^{-19}$			
	1	2	3	4
A H_2, 350°C	2.09	2.81	2.10	1.81
B O_2, 25°C	2.16	2.84	2.15	1.82

[a] A: H_2 chemisorbed at 350°C; forms $\equiv$Si—H; B: O_2 chemisorbed at 250°C, subsequent to the removal of H_2 chemisorbed in A.

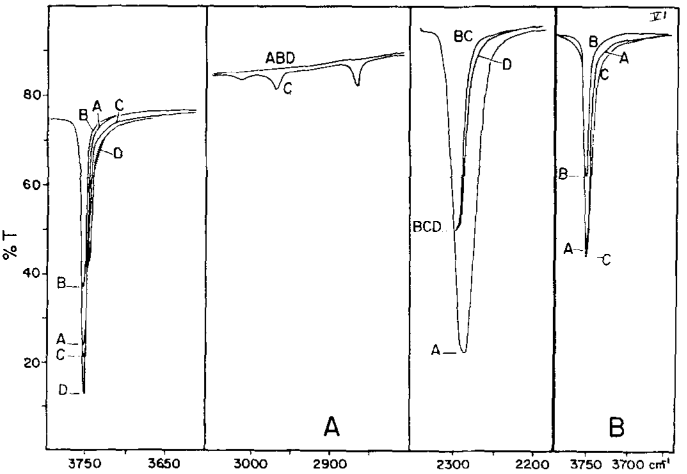
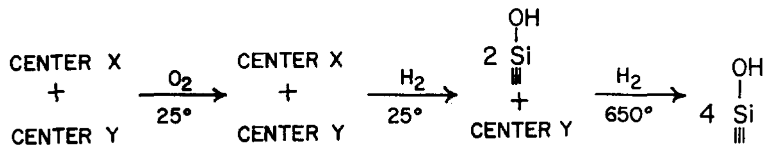


FIG. 1. H_2 Chemisorption on O_2-treated reactive silica: Part A: (A) methylated Aerosil, pyrolyzed at 800°C and treated with H_2 at 700°C for 4 hr; (B) after degassing at 830°C for 16 hr; (C) after exposure to O_2 at 25°C, degassing at 25°C, and exposure to H_2 at 25°C for 3 hr; (D) after exposure to H_2 at 600°C for 4 hr. Part B: The procedures of Part A were carried out, but with a different sample. The spectra show that the amount of Si–OH groups formed upon reaction with O_2 and H_2 at 25°C is fairly close to the amount eliminated upon degassing at 830°C.

volved center X. As the H_2/O_2 and H/O ratios of Table 2 are close to unity, it is suggested that O_2 chemisorption was also dissociative and involved only center X, and caused the conversion of the paramagnetic silicon of that center to an oxygen-containing paramagnetic center.

H_2 Chemisorption at 25°C on O_2-Treated RS

The paramagnetic center produced on RS upon O_2 chemisorption was a quite reactive one which chemisorbed H_2. The H_2 chemisorption at 25°C was complete within several minutes, after which no paramagnetic centers remained (*7*). Infrared spectroscopic data showed that the only infrared-active products of this H_2 chemisorption were surface Si–OH groups which were almost "free," i.e., they did not interact with their environment significantly (Figs. 1 and 4). The amounts of O_2, and of H_2 taken up at 25°C subsequent to the O_2 chemisorption, are shown in Table 3. The data indicate that the amounts of O_2 and H_2 taken up were very close to unity.



II

Also, as only silanols were produced, the H_2 chemisorption was dissociative and, if O_2 chemisorption involved center X and changed it to an oxygen-containing radical, the subsequent H_2 chemisorption involved the modified center X and changed the oxygen-containing radicals into silanol groups.

H_2 Chemisorption at 650°C on O_2-Treated RS

When an O_2-treated sample was exposed to H_2 at 25°C and was then heated in H_2 at 650°C, additional H_2 was taken up and the spectra show that silanols were produced. That effect is shown in the spectra of Figs. 1 and 4; the latter refer to a deuterated sample with which the reactions obviously were carried out with D_2. In particular, it is clear that at high temperatures there was no formation of silanes. The only modification of the 2300-cm^{-1} silane band (1670 cm^{-1} in the case of a deuterated sample) was a slight broadening of the low-wavenumber side of the band which might be caused by a weak interaction between silanes and the increased number of silanols or, more likely, to the decomposition of small amounts of methanol contaminant. The amounts of H_2 dissociatively chemisorbed are shown in Table 4. The data indicate that, as in the case of RS, the H_2 reacted with some oxygen-containing center which cannot include normal siloxane bridges. Presumably, that is the center Y, which remained intact when O_2 chemisorption occurred and also when H_2 chemisorbed on the O_2-treated RS. The data of Table 4, as in the case of high-temperature reaction data of Table 1, show some scatter, but the ratios of amounts of H_2 taken up at low and high temperatures are close to unity. The data may thus be summarized as follows, in analogy to Scheme I.

If, as is shown by the various data, center Y remained intact until the adsorbent was subjected to a high-temperature H_2 treatment, then all of the other chemisorptions involved only the center X. Consequently, the relations between the $\equiv$SiH, $=$SiH$_2$

TABLE 3

H_2 CHEMISORPTION AT 25° ON O_2-TREATED RS[a]

Sample	Molecules adsorbed/g, $\times 10^{-19}$ 1	2	3	4	5
A O_2, 25°	1.58	2.16	1.68	1.59	2.84
B H_2, 25°	1.73	2.19	1.64	1.44	2.80

[a] A: O_2 chemisorbed on RS at 25°C; B: H_2 chemisorbed at 25°C on the O_2-treated samples; form $\equiv$Si—OH.

TABLE 4

O_2 CHEMISORPTION AT 650°C ON O_2-TREATED RS[a]

Sample	Molecules adsorbed/g, $\times 10^{-19}$		
	1	2	3
A H_2, 25°C	1.73	1.64	1.44
B H_2, 25°C + 650°C	2.65	3.22	3.27

[a] A: H_2 chemisorbed at 25°C on O_2-treated RS; forms $\equiv$Si—OH; B: total amount of H_2 chemisorbed after 650°C H_2 treatment subsequent to H_2 chemisorption at 25°C; forms $\equiv$Si—OH.

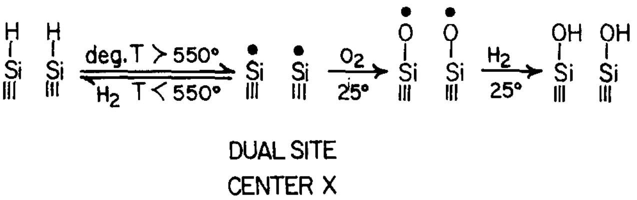
TABLE 5

CO CHEMISORPTION ON O_2-TREATED RS[a]

Sample	Molecules adsorbed/g, $\times 10^{-19}$			
	1	2	3	4
A O_2, 25°C	1.20	2.15	1.85	1.82
B CO, 25°C	1.24	2.17	1.77	1.80

[a] A: O_2 chemisorption on RS at 25°C; B: CO chemisorption on O_2-treated RS, subsequent to A.

and $\equiv$Si—OH bands, the spectroscopic data, the changes in ESR signals, and the data of Tables 1, 2, and 3 all suggest that the center X originally present on RS contained two $\equiv$Si$^\bullet$ sites. On O_2 chemisorption, pairs of $\equiv$SiO$^\bullet$ sites would be formed which would then be converted to silanols by H_2 chemisorption at 25°C. The various chemisorption reactions involving what has been termed center X can thus be represented by Scheme III:



III

CO Chemisorption on O_2-Treated RS

CO was not chemisorbed by RS. That is not unexpected, because CO has no spare electron to form a σ-bond with the silicon paramagnetic site and silicon has no *d*-electron available for back-donation to the CO. However, when RS was permitted to chemisorb O_2 and was then exposed to CO, the CO was readily chemisorbed at 25°C, the reaction being complete in a few seconds. Quantitative data are summarized in Table 5.

After the chemisorption of O_2 followed by that of CO, two new bands at 1931 and 893 cm^{-1} appeared in the infrared spectrum (Fig. 2). Bands previously present were not modified. It was possible to observe the 893-cm^{-1} band distinctly only with deuterated samples, because with regular RS samples there was another band near 885 cm^{-1} associated with the 2300-cm^{-1} band attributed to surface $=$SiH$_2$ groups (*3*) (Fig. 3). Conversion of the $=$SiH$_2$ groups into $=$SiD$_2$ groups with D_2 (*3*) eliminated the 885-cm^{-1} band which must therefore have been caused by a hydrogen-containing species. The 885-cm^{-1} band is tentatively assigned to a Si–H wagging mode (*12*). Figure 2 also shows that prolonged degassing strongly decreased the transparency of the 850–950 cm^{-1} "window" (the spectra in that region were recorded in the single-beam mode with fixed slits), two bands being formed near 890 and 913 cm^{-1} which were not due to RS but to the abundant regular silica network, as they were also formed upon degassing ordinary silica at high temperatures. The possible origin of these two bands and their disappearance upon adsorption of some molecules will be discussed elsewhere.

The 1931-cm^{-1} band is assigned to the C=O stretching mode (ν_4) of a covalent carbonate produced through the reaction of one CO molecule with two $\equiv$SiO$^\bullet$ centers. That frequency of the bridged carbonate is quite high and some 60 cm^{-1} above the upper limit usually found for covalent carbonates (*13*). However, the unperturbed C=O stretching vibration in carbon trioxide, a C_{2v} group structure similar to the

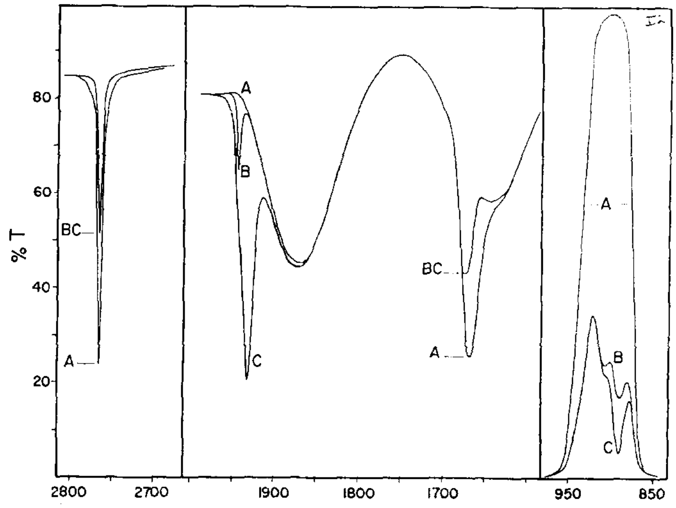


FIG. 2. CO Chemisorption on O$_2$-treated reactive silica: (A) deuterated sample after pyrolysis in presence of D$_2$ at 800°C; (B) after degassing at 830°C for 17 hr; (C) after exposure to O$_2$ at 25°C degassing at 25°C, and exposure to CO at 25°C.

covalent carbonate, has been reported at 1981 cm^{-1} (*14*) and a carbonate absorbing at 1870 cm^{-1}, bound to surface aluminum atoms, has been reported (*15*). Several factors could contribute to this frequency increase, among these being the probably high covalent character of the two Si–O bonds and also the probable strain of the O–C–O angle (*16*). Also, usually all group frequencies of species on silica are somewhat higher than those observed with the species in some other phase. The band at 893 cm^{-1} could be assigned either to the symmetrical C–O stretching, shifted to lower wavenumbers because of the same factors (*13*) mentioned above to explain the high frequency of ν_4; or to the out-of-plane vibration ν_6, the frequency of those modes being usually less reliable than that of high-frequency modes. Further support for the carbonate assignment and details about its behavior will be given elsewhere.

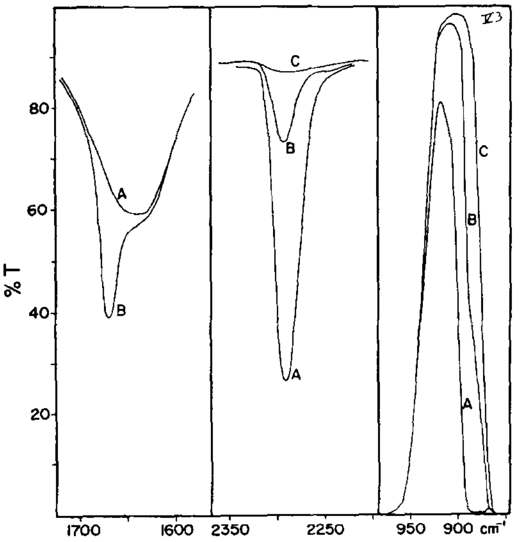
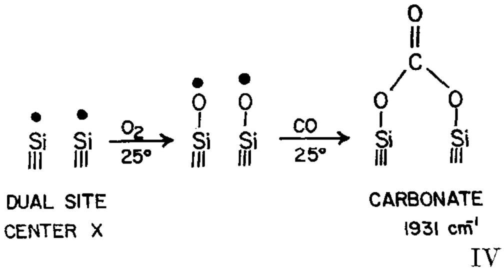


FIG. 3. Surface silanes: (A) methylated sample after pyrolsis in presence of H$_2$ at 800°C; (B) after exchange with D$_2$ at 650°C for 22 hr; (C) a fully deuterated sample; see spectrum A, Fig. 2.

The data of Table 5 indicate that one CO molecule was adsorbed for every O$_2$ molecule, i.e., one CO molecule was bound to two ≡SiO• sites which must, therefore, be closely spaced. That conclusion and the assignment of the 1931- and 893-cm^{-1} bands are mutually sustaining, and provide further support for the occurrence of dual reaction sites. The reaction of O$_2$ and subsequently of CO with RS would lead to a bridged carbonate by a scheme,



IV

The Number of Centers

The number of sites can be estimated from the adsorption data. For example, for one sample, the BET surface area after a 20-hr degassing at 800°C was 350 m^2/g, and the amount of H_2 chemisorbed at 25°C was 2.81×10^{19} molecules/g and of O_2 chemisorbed at 25°C was 2.84×10^{19} molecules/g. There were consequently 0.17 sites/100 $Å^2$ available for dissociative chemisorption, one site being capable of holding one atom. If the surface concentration of silicon atoms is taken to be either 4.6/100 $Å^2$ as on a [0001] face of β-trydimite (*17, 18*) or 4/100 $Å^2$ on a [100] face of β-crystobalite (*17, 19*), the fraction of surface silicon atoms which function as active sites is rather small. If the sites are randomly distributed over the surface, the average site-to-site distance is rather large. If two closely spaced radicals constitute the "site" or "center," the above estimate must be halved to about 0.08 dual centers/100 $Å^2$ and the center-to-center distance is increased.

The rather rapid dissociative chemisorption reactions are unusual because, if the small number of sites were randomly distributed, the relatively large average distance between sites would imply that a dissociative chemisorption was followed by a long-range diffusion of an atom over the surface. However, if the two radicals of each center act in concert, a surface diffusion is avoided. Such a dual-site pair or center is consistent with the observed quick dissociation and chemisorption of O_2 and of H_2, as well as with the previously observed formation of some acetylenic species (*2*) during the early stages of the pyrolysis of methoxylated silica.

The Nature of the Center

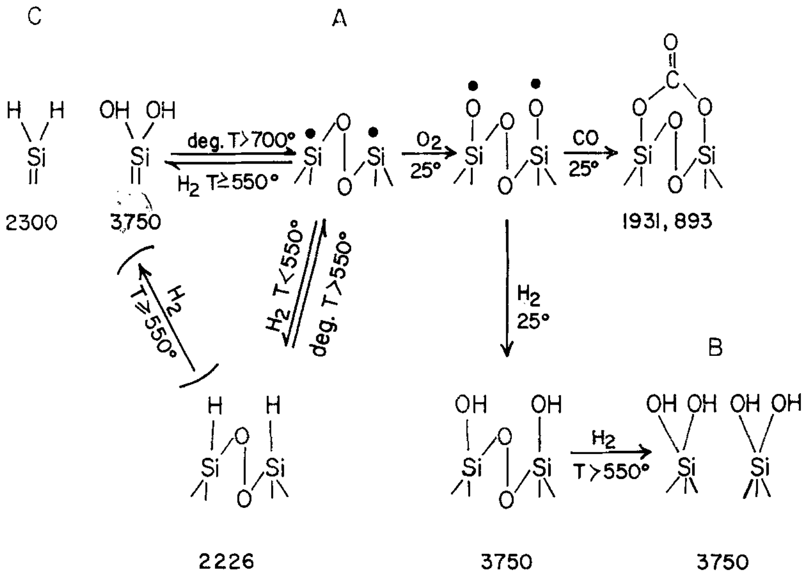
The various effects indicate that two types of reactive surface material occur on RS. One of these is the oxygen-containing material termed center Y; the other involves the paramagnetic one termed center X. Although it is possible to postulate that the 25°C O_2 chemisorption and the subsequent 25°C H_2 or CO chemisorptions involved schemes other than III or IV, e.g., the formation of a peroxo radical on one half of a pair of $Si^\bullet$ sites with subsequent rearrangement, or some cooperative effects between what has been termed centers X and Y, other postulated mechanisms and surface structures are quite complex and much more involved than is warranted in view of the data summarized by Schemes I, II, III, and IV. Indeed, those data provide strong evidence to support the view that the low-temperature chemisorptions described by Schemes III and IV involved a dual center. However, the structure of the dual center must still be considered. In fact, two neighboring silicon atoms each bearing a spare electron cannot be regarded as the dual center because two such atoms present on the regular silica framework would be approximately 5 Å apart (*17, 20*) and could not form the surface carbonate. Also, the relations between the dual center and the oxygen-containing material termed center Y must be considered.

The data of Tables 1 and 4 and the observed effects summarized by schemes I and II conclusively indicate that the high-temperature H_2 treatments consumed the same amounts of H_2 and caused the formation of the same number of hydroxyl groups. The reaction appears to be

$$\text{center Y} \xrightarrow[T > 550°C]{H_2} 2{\equiv}Si{-}OH$$

in each case, but apparently the overall reaction in Scheme I involved three silicon atoms while overall reaction sequence in Scheme II involved four silicon atoms. That disparity, as well as other complexity which arises if it is assumed that center Y is not intimately concerned with center X, is removed by postulating that the two centers form one aggregate center in which the two silicon radicals are linked to two oxygen atoms. The condition must be imposed that these oxygen atoms are not part of regular siloxane bridges because these cannot account for the high-temperature reaction with H_2. Center A of Scheme V is consequently proposed.

Center A is a composite one and thought to consist of a pair of closely spaced radicals which are responsible for the low-temperature chemisorption reactions; the



V

high-temperature H_2 reactions then involve the breaking of the peroxo-like bridge linking the site pair. The schematic representation A does not necessarily indicate a special configuration but does summarize the special properties of the center. Scheme V is a postulated one, useful in explaining the various reactions in terms of the center A, but also correctly expresses the stoichiometry previously outlined and summarized in Schemes I–IV. The action of H_2 at high temperature on the silane absorbing at 2226 cm^{-1} would not be a direct reaction as represented by the arrow within parentheses, but is the reverse of the two reactions that lead to the formation of the silane. There would be an initial hydrogen desorption step already observed in Part II of this series (*3*), and then the reaction of H_2 on the bridge, a redistribution leading to the 2300-cm^{-1} $=SiH_2$ and 3750-cm^{-1} silanols.

Although it is stressed that the schematic representation A is intended mainly to describe the properties of the center which were described earlier, the center's possible structure must be considered because that has certain implications for the products B and C of the high-temperature hydrogenation reactions.

The stoichiometry outlined in Scheme II indicates that four hydroxyls were produced and these are shown as grouping B in Scheme V. Structures A and B raise the questions: How can two adjoining pairs of hydroxyls be produced and exist without the appearance in the spectrum of even a weak perturbation indicating interactions between the silanols? If the stoichiometry is as shown in Schemes II and V, how can the existence of two oxygen atoms in between the two Si atoms constituting the site be explained?

The first question seems relatively easy to answer, because the temperature at which the second part of the reaction is occurring is higher than the temperature at which, according to Peri and Hensley's model (*19*), geminal hydroxyls condense and water is eliminated. One might consequently expect that, as soon as geminal hydroxyls are formed, water is evolved and chemisorbs on a suitable part of the surface to produce hydroxyls. This mechanism would then imply that the two Si atoms that are incorporated in the site are adjoining Si atoms on a row of the kind that is found on a [100] β-crystobalite face. However, that picture is inconsistent with the mechanism schemes. In fact, if the two Si atoms on the row were connected by a two-oxygen bridge (or peroxo bridge) as required by stoichiometry, they would be approximately 4 Å apart and would still be too far apart to hold a carbonate structure. Therefore, if it is assumed that the two Si atoms are on a row, the two oxygen atoms must be not between them but perhaps beside them. However, the condition must be imposed that the oxygen atoms must not be a part of regular strained siloxane bridges of the kind so far proposed to account for dehydration processes, because siloxane bridges alone would not explain the generation of hydroxyls by reaction with H_2 at high temperature. Conversely, one may assume that the two Si atoms are indeed connected by a peroxo bridge and that this might explain the reactivity toward H_2. However, the Si atoms must then be on different rows; in that case the two Si atoms could be brought closer together and the carbonate would not form "on top" of the peroxo bridge but "beside" it. The two different rows certainly could not be two parallel [100] β-crystobalite rows, because a connection between the atoms would bring the Si–O bonds too far away from the tetrahedral directions. The possibilities remaining are that the two rows are either perpendicular to one another, the bonding occurring between two Si atoms at a step on the [100] β-crystobalite face, or that the bonding is formed at the junction of two different crystal faces. The last is likely to be a common situation with amorphous materials in which only short-range order can be expected. In either of the above two cases the newly formed hydroxyls would remain in place, without the evolution of water, nor giving rise to an appreciable hydrogen-bonding interaction because they would not have the proper orientation to do so. The hydroxyls might indeed condense with neighboring hydroxyls, if there are any such neighbors, the evolved water forming hydroxyls on more suitable parts of the surface. However, from the spectra of Fig. 4 it is evident that the surface subsequent to the formation of deuteroxyls *via* scheme II is in a "steady state" situation as far as the position of the deuteroxyls is concerned. It is possible to decrease the 2760-cm^{-1} Si–OD band by further degassing at 800°C, but those deuteroxyls are eliminated along with $=SiD_2$ groups *via* the mechanism leading to the formation of reactive centers and are regenerated (and also the 1670-cm^{-1} $=SiD_2$ band) upon reaction with D_2 at 700°C (Fig. 4, spectrum F).

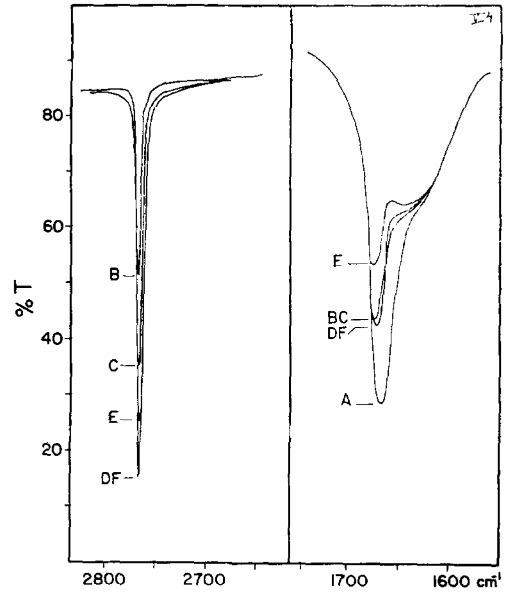
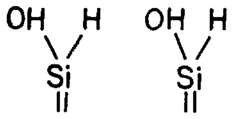


FIG. 4. Reactions with D_2: (A) methylated sample after pyrolysis in presence of D_2 at 800°C; (B) after degassing at 830°C for 17 hr; (C) after exposure to O_2 at 25°C, degassing at 25°C, and exposure to D_2 at 25°C for 14 hr; (D) after exposure to D_2 at 550°C for 23 hr and at 700°C for 5 hr; (E) after degassing at 830°C for 17 hr; (F) after exposure to D_2 at 700°C for 18 hr.

Similar considerations are pertinent for the high-temperature H_2 reaction of center A. The stoichiometry indicates that one $=SiH_2$ and two silanols were formed, and this is shown in Scheme V by the grouping C. Note that the reaction is reversible. If it is conceded that the initial formation of RS only involves the two tetrahedra which will form the center, A, and the simple stoichiometry seems to support this point of view, there are only two configurations which will lead to the center. One is structure D, provided such a structure can exist (*21*) and is not just a transient intermediate of the oxidation of the 2300-cm^{-1} species (*3*). An alternative structure is C. The high-



D

temperature reaction leading to the formation of RS would involve the elimination of hydrogen with the formation of a two-oxygen bridge between the silicon atoms, each Si bearing a free electron. We tentatively retain this description of the complex site, keeping in mind that more than two tetrahedra may be involved in its formation and that the two anomalous oxygen atoms may not be between the two paramagnetic silicon atoms but beside them. It seems not worthwhile to seek a more complete description because the centers represent only small fractions of the total silica surface and other configurations might be suggested for amorphous material.

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