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Reactive Silica

XIII. Activation of Silica by Pyrolizing Chemisorbed $HSiCl_3$[1]

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A new method of activating silica consists of chemisorbing $HSiCl_3$ and then degassing above 600°C. Infrared spectra show that surface silane groups are eliminated, and the surface is and remains completely dehydroxylated. The formation of the centers responsible for the activity probably involves the simultaneous elimination of ≡Si–Cl and =SiH_2 groups, leading to a rearrangement of the surface.

Prior work has shown that ordinary high surface area silica can be made remarkably reactive by a three-step procedure consisting of (a) a chemisorption causing the surface silanols to be replaced by another surface species, generally $-OCH_3$, (b) pyrolysing the surface layer, which resulted in the formation of ≡Si–OH and =SiH_2 groups, and (c) degassing at high temperature. Activation procedures involving a variety of adsorbates, mainly methoxy-containing materials as well as some substituted silanes, leading to the formation of reactive silica (RS) are described elsewhere (*2–5*).

In all cases the final step in the activation has been the simultaneous removal of ≡Si–OH and =SiH_2 groups, which apparently leads to a restructuring of parts of the silica surface so that the special centers responsible for the activity of RS are generated. We now describe a new procedure involving the formation of RS from completely dehydroxylated silica.

[1] Part XII, the preceding paper in this series, is Ref. (1)

EXPERIMENTAL PROCEDURES

Most experimental procedures have been described elsewhere (*1–5*). Samples for the present study were prepared by heating Cab-O-Sil pellets in O_2 at 500 to 700°C for several hours in order to remove the carbonaceous impurities usually present on the surfaces, degassing at 700 to 900°C for several hours in order to dehydroxylate the surface and, specifically, to remove all interstitial hydroxyls, and then exposing the sample to 10 to 20 Torr of $HSiCl_3$ vapor at 350°C for 0.5 hr, followed by degassing at 350°C for 0.5 hr in order to remove unreacted $HSiCl_3$. Some samples, subsequent to the high-temperature degassing required to remove interstitial hydroxyls, were rehydroxylated by heating them in water vapor at 350°C followed by degassing at 350 to 600°C, in order to obtain differing stages of dehydroxylation; the samples were then treated with $HSiCl_3$ as described.

RESULTS

The spectrum of an $HSiCl_3$-treated sample was flat in the O–H region, e.g.,

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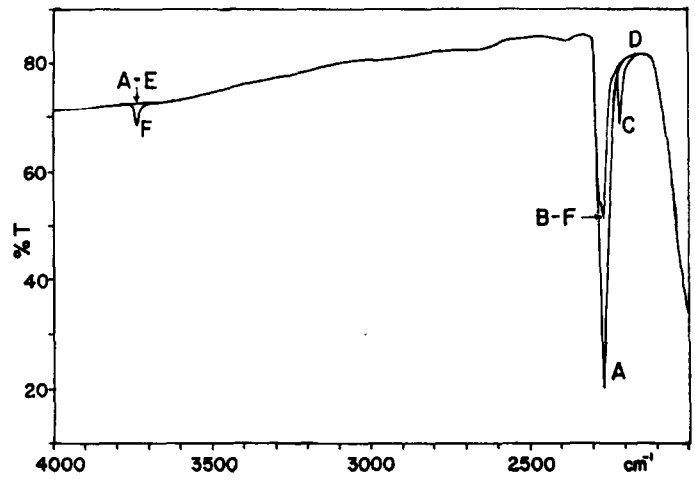

FIG. 1. Activation of $HSiCl_3$-treated silica: (A) Cab-O-Sil silica completely dehydroxylated by treatment with $HSiCl_3$ vapor at 350°C; (B) after degassing at 660°C for 1 hr; (C) after exposure to 20 Torr H_2 at 400°C for 1 hr; (D) after degassing at 650°C for 1 hr; (E) after exposure to 20 Torr O_2 at 20°C; (F) after exposure to 20 Torr H_2 at 20°C.

A in Fig. 1, and exhibited only a prominent absorption at 2270 cm^{-1} characteristic of the Si–H stretching mode. All the interstitial hydroxyls had been removed previously, and the surface hydroxyls had been replaced, the main reaction apparently being (*6*)

$$\equiv Si\text{–}OH + HSiCl_3 \rightarrow \equiv Si\text{–}O\text{–}SiHCl_2 + HCl.$$

When the sample was degassed in the 500 to 600°C range, the silane band shifted to 2277 to 2280 cm^{-1} and then decreased in intensity upon degassing above 600°C (B, Fig. 1); details concerning the reactivity, decomposition, and rearrangement of the $\equiv Si\text{–}O\text{–}SiHCl_2$ layer will be given elsewhere.

When the sample was exposed to H_2, a band was formed at 2226 cm^{-1} (C, Fig. 1), there being no other changes in the spectrum. That band could be eliminated by degassing in the 550 to 600°C range (D, Fig. 1). Experiments with other samples showed that the band could be restored by reexposing the sample to H_2, so that the H_2 chemisorption was reversible.

If the sample was exposed to O_2 (subsequent to the adsorption–desorption steps indicated by traces C and D of Fig. 1), there were no changes in the spectrum (E, Fig. 1). Exposing that sample to H_2 then led to the formation of a small band at 3748 cm^{-1} (F, Fig. 1), indicating that some $\equiv Si\text{–}OH$ groups had formed.

Exposing a sample which was active (but had not been exposed to O_2) to NH_3 led to the formation of bands at 3530 and 3448 cm^{-1}, indicating the presence of surface $\equiv Si\text{–}NH_2$ groups, and a silane band at 2246 cm^{-1}.

Heating an active sample in H_2 above 700°C, or heating a sample in H_2 so that the 2226 cm^{-1} species formed (equivalent to the stage represented by C of Fig. 1) and then heating in H_2 above 700°C, resulted in the formation of 3745-cm^{-1} $\equiv Si\text{–}OH$ and 2280 to 2290-cm^{-1} $=SiH_2$ bands.

The band assignments are summarized in Fig. 2. The assignments and surface structures shown are based on results obtained with RS and are given in detail elsewhere (*2*, *5*). The schematic structure I summarizes the properties of the RS center.

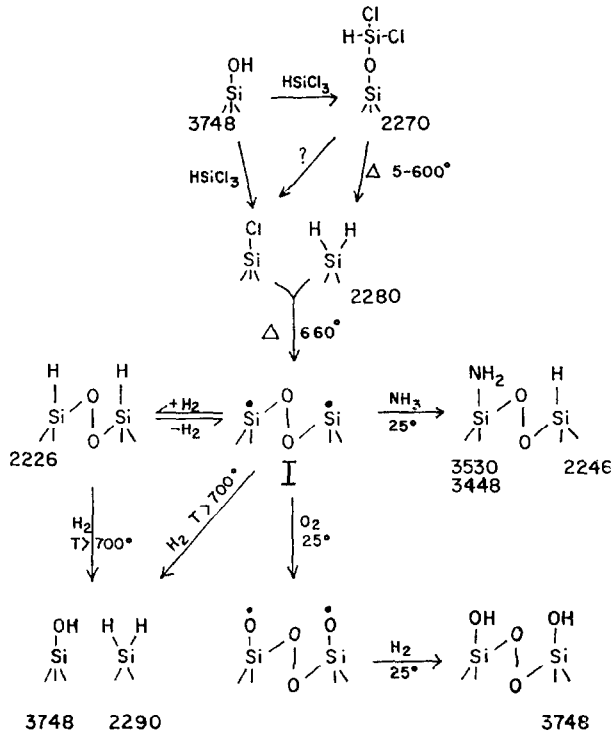

FIG. 2. Summary of experiments, observations, and mechanisms.

DISCUSSION

The experiments and observations outlined above are summarized in Fig. 2. These results are exactly the same as those obtained with RS (*2*, *5*) and thus show that RS can be prepared by degassing $HSiCl_3$-treated silica. A new method of preparing RS is thus available. Of greater interest, however, is the unusual mode of formation of the RS center, without the presence of hydroxyls.

The ingredients from which the RS center might be formed include $\equiv Si–O–SiHCl_2$, possibly some $(\equiv Si–O)_2SiHCl$ or even $(\equiv Si–O)_3SiH$ species, some condensation products formed from $\equiv Si–O–SiHCl_2$ during the pyrolysis, the $=SiH_2$ species, and the siloxane bridges. The latter can be discounted because of their lack of reactivity: it is possible to form RS by heating silica in H_2 and degassing (*7*, *8*), but very high temperatures for prolonged periods are required and the reaction is not at all extensive. In contrast, the activation of $HSiCl_3$-treated silica occurred fairly rapidly (~1 hr at 650°C) at appreciably lower temperatures than usual (with samples containing $\equiv Si–OH$ and $=SiH_2$ groups produced by pyrolysing methoxylated silica, several *days* of degassing at 750°C are needed). Thus, the mixture of $\equiv Si–OH$ and $=SiH_2$ groups is appreciably more stable than the mixture of $=SiH_2$ plus whatever groups are present on the pyrolysed, silane-treated surfaces. Or, the latter contain groups which are less stable or more mobile than silanols, so that the reaction with $=SiH_2$ and rearrangement of the surface to form I becomes easier. Such groups might be surface $\equiv SiCl$.

Work dealing with the chemisorption of various halogenated silanes on silica, recently reviewed by Hair (*9*), has shown that the silane-treated samples contained more chlorine than could be accounted for by the reaction with silanols and that the

kinetics were peculiar, suggesting the formation of ≡Si-Cl groups. Such groups, formed in the present experiments during the $HSiCl_3$ chemisorption or during the pyrolysis of the chemisorbed layer, may be involved in the present experiments, i.e., the activation step was,

$$2{\equiv}Si{-}Cl + {=}SiH_2 \rightarrow \mathbf{I}.$$

The lower temperature and faster rate at which activation occurred are in line with the relative bond strengths (Si–O, 108; Si–Cl, 91; Si–N, 85; Si–Br, 74; Si–I, 56 kcal/mol (*10*)), i.e., suitable-spaced ≡SiCl groups would be disrupted and react with $=SiH_2$ groups more readily than ≡SiOH groups. Unfortunately, infrared bands of the Si–Cl stretching modes fall in a region of the spectrum where usable samples are opaque, and laser Raman spectroscopy was unable to detect Si–Cl species (*11*), so that the participation of ≡Si–Cl species cannot be directly shown at present.

It seems likely that other surface species containing Si–halogen or Si–N bonds would take part in the rearrangement of a portion of the silica surface leading to the formatioy of **I**, and there might also be substitutes for $=SiH_2$, so that activation might occur at even lower temperatures. Parenthetically, such "activation" might be a more general phenomenon occurring on other solids, i.e., the simultaneous removal of two suitable species might lead to the formation of catalytically active sites.

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