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Reactive Silica

VI. Evidence for the Existence of a Dual Reaction Center Involving Ṡi–Ȯ Pairs*

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Extensive work has pointed to the existence on the surface of reactive silica [Morterra and Low, *J. Catal.* **28**, 265 (1973)] of a dual reaction center having the properties expected of a pair of closely spaced Ṡi sites associated with two anomalously reactive oxygen atoms; that center could be converted to another apparently containing SiȮ pairs. Evidence based on some of the reactions of these centers is now used to postulate the existence of a third center consisting of an SiȮ–Ṡi pair.

INTRODUCTION

Reactive silica (RS) is a novel adsorbent which can be produced by methoxylating high surface area silicas, pyrolyzing the methoxy layer, and then removing surface silanes and silanols formed during the pyrolysis. The adsorbent produced in this fashion is not merely highly "active" in comparison to ordinary silicas but is capable of chemisorption reactions completely unlike those which have been reported to occur on ordinary silicas. The new reactions and new surface species formed with RS, which are described in detail elsewhere (*1–7*), have led to a novel and interesting aspect of the chemistry of silica surfaces.

Extensive work on the chemisorptions of H_2, O_2, CO, H_2O, NO, CH_4, NH_3, and $(CN)_2$ has provided compelling evidence that the "activity" of RS is caused by special reaction centers which are formed after a silica has been subjected to the three-step activation procedure. The properties of the center are summarized by the schematic formulation A in Fig. 1, i.e., those of a center consisting of a pair of closely spaced silicon radicals, the pair being associated with two anomalously reactive oxygen atoms. It is stressed that A summarizes the properties of the center but implies little about its geometry beyond the requirement that the two radicals must be closely spaced.

Some of the low-temperature chemisorption reactions which have been studied are shown in Fig. 1. The latter only outlines the salient features; details are given elsewhere (*7*). The structures A to G are based on infrared spectroscopic studies. Figure 1 also correctly expresses the stoichiometry of the reactions (except for reaction II), based on quantitative gas adsorption measurements. All these reactions, including others which it is not pertinent to consider at present, involve the RS dual center A or the dual oxo center D which is produced by reaction III, i.e., by exposing freshly prepared RS to O_2 at 25°C and evacuating the reaction cell at 25°C in order to remove excess O_2. It has been found, however, that these well-defined and well-established reaction paths were apparently not followed under certain circumstances. A third reaction center seemed to be involved. The purpose of the present paper is to consider the possible nature of this third species.

RESULTS AND DISCUSSION

Some experimental data which point to the existence of a third reaction center are

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* Part V: Ref. (*6*).

shown in Figs. 2, 3, and 4. In each case, the left portion of the figure outlines the observations which have been made using infrared spectroscopy; the right portion describes the mechanism proposed to account for the observations.

Figure 2 shows some results which were obtained with RS which had been exposed to O_2 (reaction III) and then to NO (reaction VI). After the species G had been formed, the adsorbent was degassed and subjected to the treatments indicated on the left portion of Fig. 2. In the latter, and also in Figs. 3 and 4, the symbol [?] is used to indicate the surface in its degassed state.

Degassing caused species G to disappear. Exposing the degassed surface to NO caused some but not all of the species G to reform, judging by the relative intensities of the appropriate infrared bands. These results would indicate that reaction VI was partially reversible, i.e., that, as shown on the right side of Fig. 2, there had been some desorption of NO (reaction −VI), some of the species D being formed. When the degassed adsorbent was exposed to H_2 at 25°C, however, the infrared spectra indicated that species C and E were formed. The formation of species E would be a "normal" reaction occurring as a consequence of the desorption step −VI, i.e., the normal reaction IV would occur because some species D had been formed, so that the conversion of D to E could occur. The reaction to form species C would thus be an "abnormal" reaction.

Species C, which had been formed along with species E, would normally be formed by the reaction of water with center A, i.e., via reaction II of Fig. 1. As water was not involved in the experiments outlined in Fig. 2 (Pd-diffused H_2 was used, and the interfering effects of water were not observed in a variety of experiments connected with the experiments of Fig. 2, so that the possi-

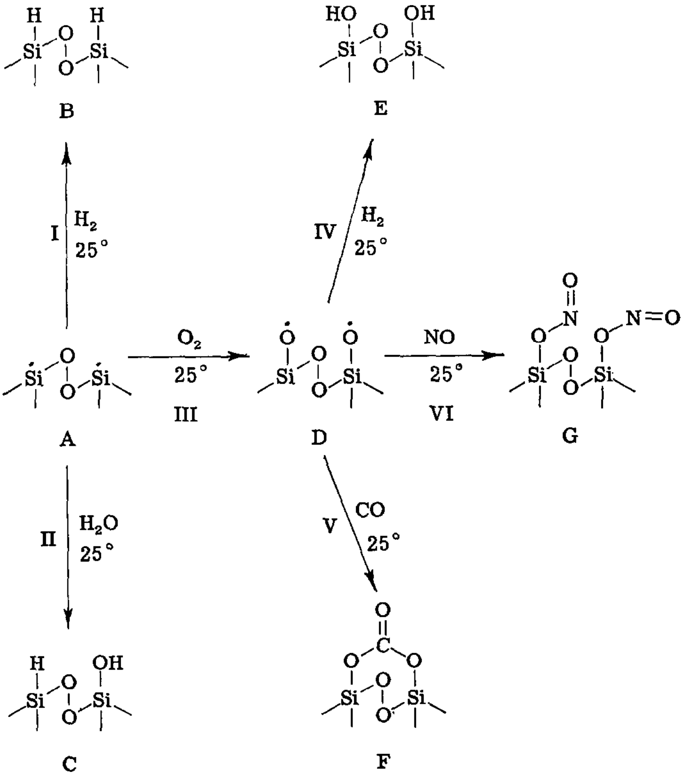


FIGURE 1

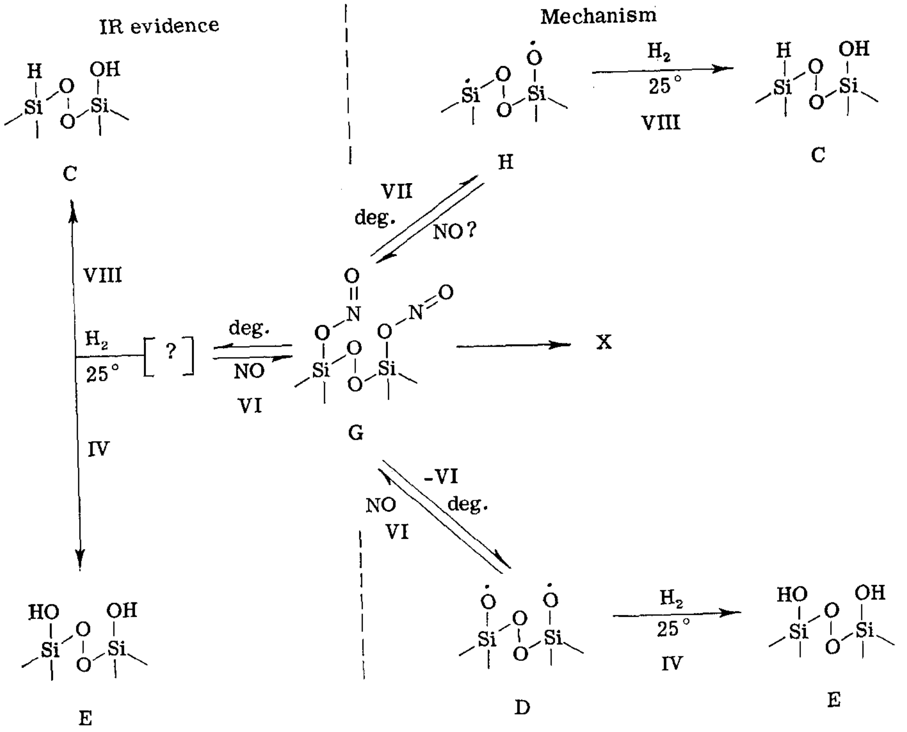


FIGURE 2

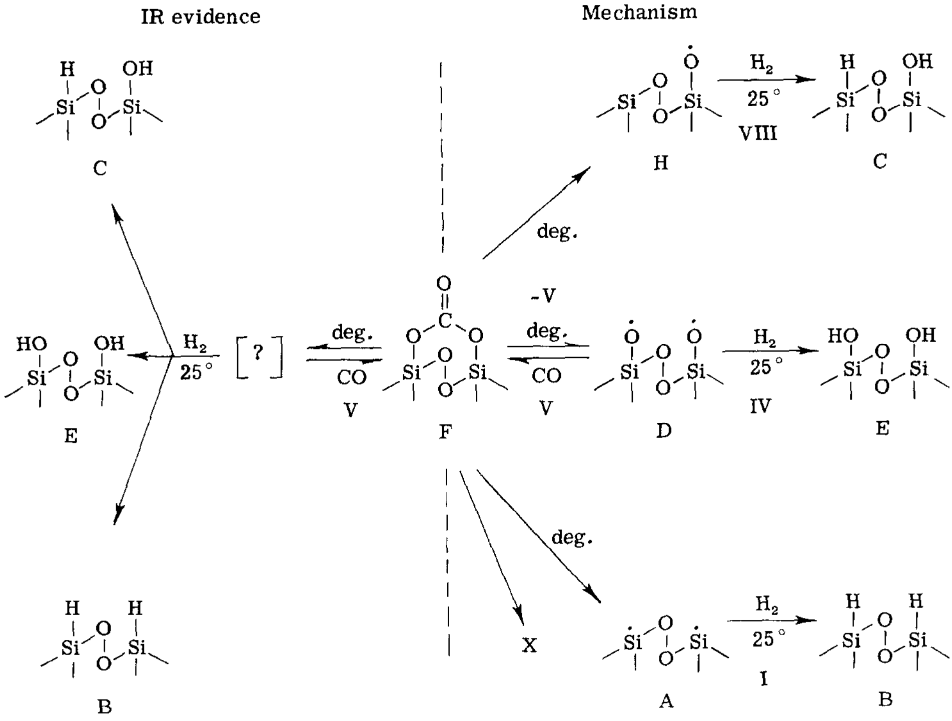


FIGURE 3

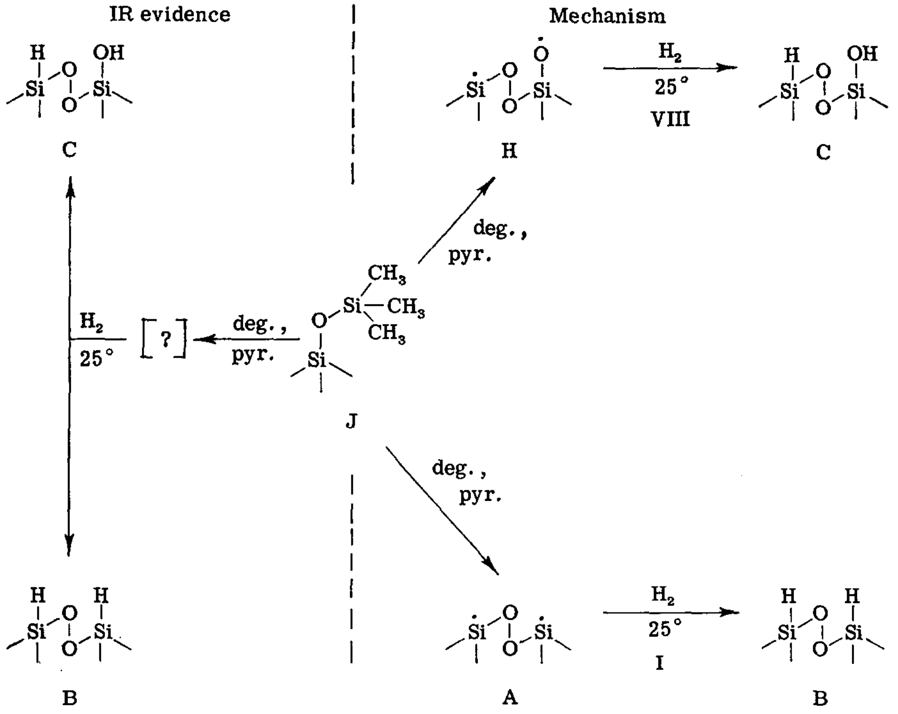
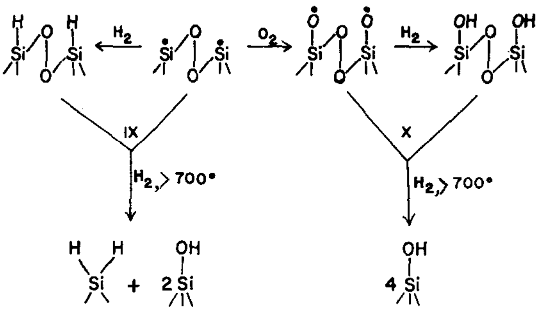


FIGURE 4

bility of the presence of water impurity need not be considered), it is necessary to postulate a new reaction center H to account for the observed reaction VIII leading to the formation of species C. The observations thus suggest that when species G were removed by degassing, the degassed surface contained a mixture of centers D and H (as well as some structure X, which is considered below). Exposure to H_2 would then lead to the normal reaction IV, as well as to the abnormal reaction VIII to form structure C.

Similar although more complex results were obtained with RS samples which had been oxygen-treated, permitted to chemisorb CO, and then degassed (Fig. 3). Exposing the degassed surface to H_2 led to the formation of species B, C, and E. The observations point to the occurrence of two normal reactions (I and IV) and to the occurrence of the abnormal reaction VIII involving the postulated new center H. The degassed surface would thus have contained a mixture of species A, D, and H as well as some species X, the latter again being introduced to account for some irreversibility of reaction V.

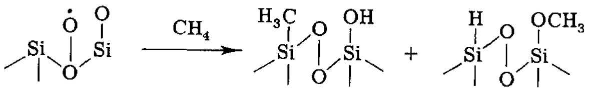
The low-temperature chemisorptions shown in Fig. 1 involve the two silicon sites and the integrity of the center is retained. At high temperatures, however, additional reactions occur. These have been clearly identified only for the reactions with H_2, and are



The high-temperature reaction IX or X, during which the integrity of the reactive center A or D was lost, occurs with the other species shown in Fig. 1. There were also some deactivation reactions; e.g., the NO reaction VI was only partially reversible. The degassing reactions, which lead to a partial lack of "activity," probably involved a loss of integrity of the site configuration similar to that which occurred during the high-temperature H_2 reactions IX and X. To account for such deactivation, the structure X has been incorporated in Figs. 2 and 3.

Some additional evidence supporting reaction VIII and center H comes from the experiments outlined in Fig. 4. Silica had been reacted with $ClSi(CH_3)_3$ so that the structures J were formed. When the sample was pyrolyzed and degassed (in an attempt to prepare RS by a method other than the methoxylation procedure described earlier) and then exposed to H_2, species B and C were formed (left portion of Fig. 4). The results again suggest the occurrence of the normal reaction I plus the abnormal reaction VIII; i.e., the pyrolyzed and degassed surface contained the usual RS center A and the newly postulated center H.

The dissociative chemisorption reactions I, II, III, and IV occurred readily and the analogous reaction VIII, which involves a simple scission of H_2 molecules similar to, say, that in reaction IV, is consequently not a strange one. Also, the postulated half-oxygenated dual center H is very similar to the basic RS dual center A and to the fully oxygenated RS center D, and is not an unreasonable structure. It seems probable that electron spin resonance experiments would help to characterize the center. Certainly, a center such as H is needed to explain the formation of species C, and it seems likely that other interesting reactions could occur, e.g.,



It seems, however, that center H was not formed by a direct reaction; i.e., there is no evidence at all for a stepwise sequence by which center A first converted to center H and then to center D. Apparently, center H could only be formed by the decomposition of a complex species such as F or G.

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