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Reactive Silica

X. Ethylene Sorption and Polymerization[1]

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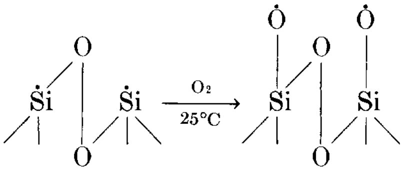
A variety of data indicates that unusual adsorption centers containing silicon radicals are formed when high surface area silicas are subjected to an activation procedure consisting of methoxylation, pyrolysis of the methoxy layer, and high temperature degassing. The reactive silica (RS) adsorbent can chemisorb oxygen, the oxygenated reactive silica (ORS) containing SiO radicals. To test the capability of the radical centers of RS and ORS to act as initiators for free radical initiated chain reactions, the sorption of ethylene by RS and ORS was studied using infrared spectroscopic techniques. The data indicate that several tightly bonded surface structures were formed, including polyethylene.

INTRODUCTION

If ordinary high surface area silicas are methoxylated and then pyrolized and degassed at high temperatures, the silicas become remarkably active in chemisorbing a variety of gases; and surface structures unlike those found on ordinary silicas are formed. The activity of such especially treated adsorbents, which are termed reactive silica (RS) for brevity, are thought to arise from the presence on the silica surface of unusual reaction centers, shown schematically as structure **I**. The latter summarizes the properties of the center, i.e., those of a pair of silicon radicals associated with two anomalously reactive oxygen atoms, but infers little about the geometry besides the requirement that the two silicons be closely spaced. Data pointing to the existence of the dual center **I** and about the chemisorption properties of RS are detailed elsewhere (*1–11*).



I
RS center

II
ORS center

The radical nature of the postulated RS center **I** is a highly unusual one for an adsorption site, and it can be argued that if whatever site or center is responsible for the highly unusual surface properties of RS is radical, then the surface-bound radicals should function as initiators of radical-propagated chain reactions. Similarly, the center **II**, produced by exposing RS to O_2 to yield ORS (oxygen-treated RS) (*6, 7*) should also be active as initiators. In this view, the centers **I** and/or **II** should act as initiators for the free radical polymerization of ethylene (*12–14*). To test this thesis and to provide information about the properties of RS and ORS, we have

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studied some aspects of the sorption of ethylene by RS and by ORS using infrared spectroscopic techniques.

EXPERIMENTAL METHODS

Most experimental procedures have been described elsewhere (*2*, *3*, *7*, *10*). Cab-O-Sil silica (*15*) was converted to RS using methyl orthoformate (*10*). ORS was prepared by exposing RS to several tens of Torr of O_2 at 25°C for several minutes and then removing the residual O_2 by pumping to $\sim 10^{-5}$ Torr.

Ethylene (*16*) "pure grade" was degassed at liquid nitrogen temperature and distilled several times prior to use.

RESULTS AND DISCUSSION

When RS samples were exposed to ethylene at room temperature (nominally 25°C), there were changes in the C–H regions of spectra. (The first spectrum was recorded about 5–10 min after letting the gas into the cell, i.e., a period long enough to carry out the manipulation involved in getting the cell from the vacuum system to the spectrometer and scanning the spectrum.) Small bands at 2967, 2920, and 2850 appeared (B, Fig. 1), shifted to 2925 and 2857 cm^{-1}, and increased in intensity, the increase decelerating and ceasing after about 2 days. After long exposure times very weak bands were noticeable at 3059 and 2989 cm^{-1}. The 3748 cm^{-1} ≡Si–OH band was not affected except that, after long exposure, a weak tailing was observed (D, Fig. 1). The Si–H range was not affected by the ethylene sorption. After the growth of the C–H bands had stopped, increasing the ethylene pressure had no effect.

Degassing had no significant effects until 200°C was reached, when the 3059 and 2989 cm^{-1} bands disappeared. There was a barely noticeable decrease of the 2925 and 2857 cm^{-1} bands upon degassing at 300°C, a minor absorption appeared near 2200 cm^{-1} and the contour of the 2967 cm^{-1} band changed. These changes continued until 400°C was reached, when two bands appeared near 2225 and 2212 cm^{-1} (C, Fig. 2). Further changes occurred upon degassing at 500°C (E, Fig. 2) in that the 2925 and 2857 cm^{-1} bands decreased markedly, the 2967 cm^{-1} band split into two bands at 2975 and 2963 cm^{-1}, and a weak band appeared at 3046 cm^{-1}. There were no significant changes in the ≡SI–OH band.

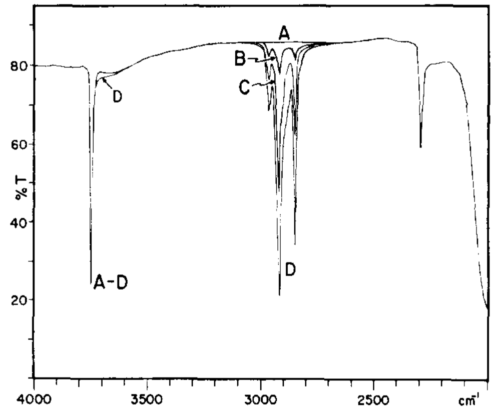


FIG. 1. Ethylene sorption by RS. After the background spectrum A had been recorded, the sample was exposed to 7 Torr of ethylene at 25°C for ~10 min (B); 15 hr (C); and 2–6 days (D).

Somewhat more complex results were obtained with ORS. When an ORS sample was exposed to ethylene (Fig. 3), there were rapid changes in the O–H region, an intense absorption consisting of two overlapping bands at 3747 and 3740 cm^{-1} appearing (B, Fig. 3), along with a series of bands in the C–H region at 3061, a shoulder at ~3008, 2991, 2976, a shoulder near 2920, a sharp band at 2908, and a weak band at 2858 cm^{-1}. The major C–H bands changed only slightly, and the 3740 cm^{-1} increased slightly, upon prolonged exposure to ethylene, but the 2925 and 2858 cm^{-1} bands grew significantly. As with RS, the growth decelerated, and there were no significant changes after about 2 days. The Si–H region was not affected.

Degassing caused no changes until 300°C, when the 3061 and 3008 cm^{-1} bands dis-

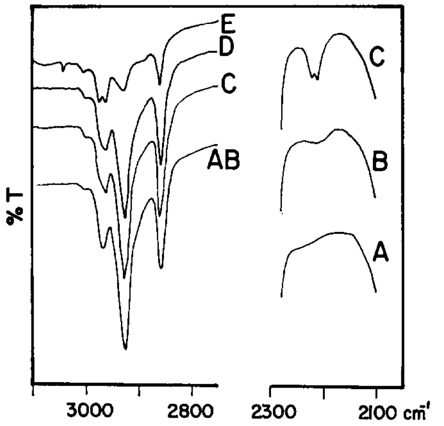


FIG. 2. Desorption: Ethylene/RS. After being exposed to 4 Torr of ethylene at 25°C for 2 days (A) the sample was degassed for 0.5 hr at 300°C (B); 400°C (C); 450°C (D); and 500°C (E). The ordinates are displaced.

appeared, the 3740 cm^{-1} band merged with the 3747 cm^{-1} band, so that the whole ≡Si–OH band increased in intensity. There were no further changes until 480°C was reached, when all bands decreased, the rate of decline of the 2925 and 2858 cm^{-1} bands being greater than that of other bands. All C–H bands continued to decrease as the temperature was raised, accompanied by an increase of the ≡Si–OH band (E–H, Fig. 3). Judging by the relative band intensities and the rates of appearance and disappearance of bands, the surface layer consisted of a mixture of at least three components, i.e., the species absorbing at 3061 and ~3008 cm^{-1}, that absorbing at 2991, 2976, and 2908 cm^{-1}, and a third species absorbing at 2925 and 2858 cm^{-1}.

The results obtained with the two adsorbents showed some similarities in that in each case (i) fairly tightly bound species were formed, as shown by the relatively high stability of the surface layer to degassing; (ii) dehydrogenation of the ethylene occurred, as indicated by the formation of hydroxyls in the case of ORS and by the 2967 cm^{-1} band attributable to methyl groups in the case of RS; (iii) there was the decelerating growth of a species absorbing at 2925 and 2858 cm^{-1}; and (iv) there was no clear evidence suggesting the bonding of only a single ethylene molecule to both sites of an RS or ORS center. Consideration of all the data, including the band frequencies and relations between band intensities, supports the following interpretation.

The 2967, 2925, and 2857 cm^{-1} bands found with ethylene sorption on RS (Fig. 1; A, Fig. 2) clearly are attributable to aliphatic methyl and methylene stretchings (*17–19*), the pair of bands at 2925 and 2857 cm^{-1} being at or near the frequencies of bands attributed to the asymmetric and symmetric C–H stretching bands of the $-CH_2-$ groups of polyethylene (*20–22*). It is thus reasonable to conclude that the sorbed layer on RS (Fig. 1; A, Fig. 2) consisted mainly of aliphatic species. There is no evidence pointing to the existence of species having "saturated" carbons such as $Si-CH_2-CH_2-Si$, or for large numbers of olefinic species such as $Si-CH=CH_2$, which would show absorptions above ~3000 cm^{-1}. However, the C–H regions of the spectra of the sorbed ethylene are unlike published spectra of polyethylenes (e.g., *18–24*) in that the present spectra indicate the presence of a significant fraction of CH_3 groups. There is thus some similarity to the spectra of ethylene sorbed by supported metals and oxides (*25, 26*); $-CH_3$ groups were found then, indicating that self-hydrogenation had occurred, and polymerization of ethylene into groups larger than $-CH_2-CH_3$ groups was suggested.

It is possible to obtain estimates of the relative numbers of $-CH_3$ and $-CH_2-$ groups from the relative intensities of the 2967 and 2925 cm^{-1} bands, keeping in mind the uncertainties (*25, 26*) present. Series of spectra recorded after different exposure times show the CH_2/CH_3 ratio to increase with increasing exposure time and increasing total sorption. For example, for the series of Fig. 1 (not all traces are shown), the CH_2/CH_3 ratio for trace A, recorded after 5–10 min, is ~1.6, becomes ~2.7 after

1 hr, about 4.4 after 15 hr, and reaches a maximum of about 5.9. A CH_2/CH_3 value of ~1 is obtained by extrapolating the crude estimates to short sorption times. The final CH_2/CH_3 ratio attained also varied with the activity of the sample. For example, with the sample of modest activity, in terms of the total amount sorbed, the CH_2/CH_3 ratio is ~3.8 (A, Fig. 2); with a sample of high activity, it is ~5.9 (D, Fig. 1). The results thus indicate, in the absence of significant quantities of olefinic species, that some self-hydrogenation occurred and that the nature of the sorbed layer changed as the sorption proceeded, ethylene molecules adsorbing during the latter stages of reaction leading to the formation of more $-CH_2-$ groups than during the initial stages. As all RS centers have the same "activity," a suggestion that highly active sites reacted faster than less reactive sites, as may be the case with atoms on different planes of a metal surface, so that the different surface products may be obtained depending on the "strength" of the site, seems implausible. The reaction scheme of Fig. 4 is suggested to account for the results.

The reaction leading to **III** involves the adsorption of more than C_2H_4 unit and leads to self-hydrogenation, i.e., a C_2H_4 molecule is stripped of hydrogen, leaving a residue indicated schematically by C_n on or near the center. The structure **III** is then deactivated. The residue would be much like the surface "carbide" formed during the sorption of acetylene and ethylene on metals (*25, 26*). Another sorption involves the binding of ethylene molecules onto the primary adsorption sites of **I** and then onto secondary sites such as **IV** and **V**, followed by further adsorption to lead to the polymer shown schematically as $(CH_2)_n$, this being equivalent to a free radical polymerization reaction (*12–14*). The absence of significant absorptions attributable to vinyl groups suggests that in the present case the chain termination by disproportionation was not as important as recombination reactions (*12–14*). It is interesting to note that in the present case the trend toward increasing CH_2/CH_3 ratios is the same as that found in the bulk process of ethylene polymerization, i.e., as chain length increased, chain branching decreased (*12–14*).

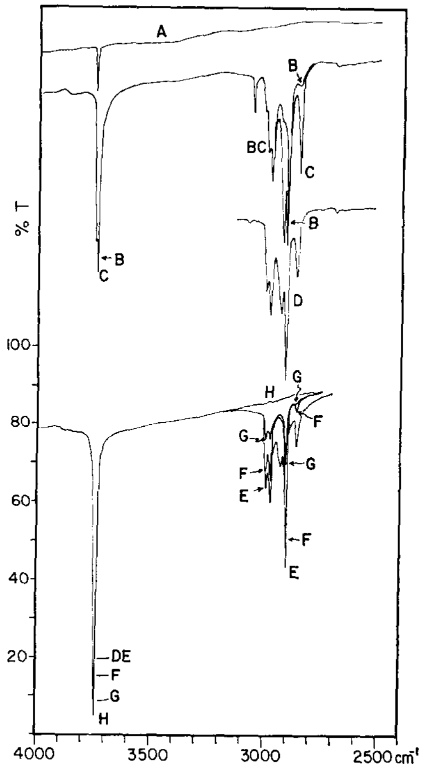


FIG. 3. Ethylene sorption–desorption by ORS. After the background spectrum A had been recorded, the sample was exposed to 7 Torr ethylene at 25°C for ~10 min (B); and 2 hr to 2 days (C). The sample was then degassed at increasing temperatures including 1 hr at 480°C (D); 5 hr at 480°C (E); 0.5 hr at 550°C (F); 0.5 hr at 640°C (G); and 0.5 hr at 750°C (H). Some ordinates are displaced.

The somewhat more complex results obtained with ORS (Fig. 3) can also be accounted for by chain processes, leading to $(CH_2)_n$ via **VI** and **VII** but it is apparent that there were two general steps, i.e., the initial and rapid growth of the species responsible for the production of silanols and the two species absorbing at 3061 and

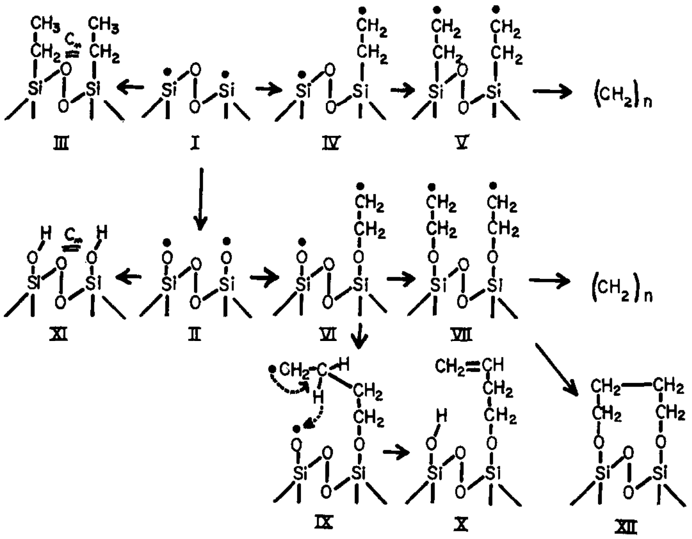
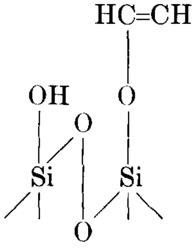


Fig. 4. Postulated reaction scheme for ethylene sorption on RS.

3008 cm^{-1} and at 2991, 2976 and 2908 cm^{-1}, and a slow growth of the 2925, 2858 cm^{-1} species. The following is suggested.

The 3061 and 3008 cm^{-1} bands, going by group frequencies (*16–18*) can be attributed to olefinic C–H vibration, i.e., to vinyl, vinylidene, and $CR_1R_2{=}CHR_3$ structures. As both absorptions appear and disappear together, vinyl groups seem likely, possibly generated by a dissociative adsorption of ethylene to form structure **VIII**:



VIII

this would also account for the formation of hydroxyl groups. However, the $-O-CH{=}CH_2$ group of **VIII** resembles a "half" of $H_2C{=}CH{-}O{-}HC{=}CH_2$, for which $\nu_{as}(CH_2)$ is at 3124 cm^{-1} and $\nu(CH)$ is at 3038 cm^{-1} (*27*); the presence of the oxygen apparently causes $\nu_{as}(CH_2)$ to shift to a frequency higher than the usual 3095–3075 cm^{-1} range (*17*). As the 3061 cm^{-1} band is ~60 cm^{-1} too low for **VIII**, it seems better to postulate a structure **X** formed via structure **IX**. The $-CH_2-$ groups of **X** would contribute to the absorptions in the 2925 and 2858 cm^{-1} region, with $\nu(CH) \sim 3008$ cm^{-1}; and the silanol, perturbed by the neighboring chain, absorbing at 3740 cm^{-1}. Some partial support for **X** comes from the observation that the splitting of the silanol band disappeared when degassing caused the 3061, 3008 cm^{-1} bands to disappear.

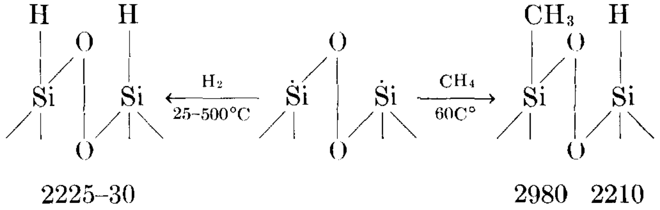
Although the formation of **X** can account for the generation of some hydroxyls, an additional hydroxyl-generating mechanism seems necessary to account for the large ≡Si–OH band. It is suggested that ethylene dehydration occurred, i.e., **XI** formed, the C_n schematically indicating "carbide" in analogy to **III**. The main reactions of RS and ORS are thus quite similar.

The 2991, 2976 cm^{-1} bands are near the frequencies of the methyl stretching bands of ethoxy and *sec*- or *tert*-butoxy groups (*17, 28*), but other bands near 2935 and 2880–70 cm^{-1} present in spectra of the alcohols (*27*) are missing in the spectra of the sorbed ethylene (Fig. 3), and the spectra recorded at various stages of degassing indicate that the 2991 and 2976 cm^{-1} bands are related to the 2908 cm^{-1} band, i.e., the three bands arise from a single species. The observed bands are either too high or too low in frequency for "normal" methyl or methylene groups, and there are too few bands for alkoxydes; if the split absorption (2991–76) is considered as one band, then only two bands are available.

The structure **XII** is tentatively advanced to account for the 2991, 2976, and 2908 cm^{-1} bands, i.e., $-CH_2-$ bands shifted to higher frequencies because of the effects of the oxygen within the structure. By analogy, the C–H bands of γ-butyrolactone, which contains only $-CH_2-$ groups, are shifted from the "normal" 2926–2853 cm^{-1} range to ~2995 and 2920 cm^{-1} (*23*). In forming via **VII**, the combination reaction leads to chain termination and a deactivation of the radicals.

The remaining pair of bands at 2925 and 2858 cm^{-1} are attributed to $-CH_2-$ groups as in the case with RS. Bands attributable to methyl and vinyl groups were not observed, suggesting that chain branching and chain termination by disproportionation of relatively short chains was not significant, i.e., the chains were relatively long so that methyl and vinyl groups associated with them were few and their absorptions too weak to observe. What is implied is that the initial rapid sorption of ethylene led to the formation of a surface layer consisting of a mixture of structures such as **X**, **XI**, and **XII**, so that the surface was largely deactivated. Adsorption could then continue on a few structures such as **VII**, these being randomly distributed, leading to the formation of $-(CH_2)_n-$ chains which were relatively unbranched and far apart, i.e., linear polyethylene.

It is interesting to note that apparently a "simple" dissociation whereby a fragment was bound to each of the two sites of the dual center, as in **VIII**, did not occur upon adsorption. For example, H_2 chemisorption was thought to lead to a silane **XIII** absorbing at 2225–30 cm^{-1} (*6*) and CH_4 sorption to **XIV** absorbing at 2980 and 2210 cm^{-1} (*7*). However, the changes in the spectra observed on degassing ethylene-treated RS (Fig. 2) suggest that such structures were formed. At the higher degassing temperatures two overlapping bands near 2225 and 2212 cm^{-1} were formed and the 2967 cm^{-1} CH_3 band showed splitting at ~2975 and 2963 cm^{-1} (C, E, Fig. 2). Considering that there may be small shifts in frequencies because of the overlapping, the 2225 cm^{-1} band can be attributed to structure **XIII**, and the 2975, 2212 cm^{-1} pair to structure **XIV**.



XIII **I** **XIV**

There was also an increase in the silanol band when the ethylene-treated ORS was degassed (D–H, Fig. 3), indicating the formation of additional structures **XI**. The mechanism of formation of **XIII** and **XIV** and **XI** from the structures are not clear.

ACKNOWLEDGMENT

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