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Surface Structure and Catalytic Cracking Properties of the SiO_2/BCl_3, $SiO_2/AlMe_3$, and $SiO_2/AlCl_3$ Systems

I. Infrared and Analytical Studies

R. J. PEGLAR, F. H. HAMBLETON, AND J. A. HOCKEY

Chemistry Department, University of Manchester Institute of Science and Technology, Manchester, M60 1QD, England

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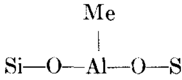
The reactions of boron trichloride, aluminum trichloride, and aluminum trimethyl vapors with the surfaces of characterized Aerosil silicas have been studied using infrared, mass spectrometric, and gravimetric techniques. Boron trichloride reacts completely with both the single and hydrogen-bonded surface hydroxyls. Exposure of the reacted solid to water vapor results in the reformation of the single SiOH groups and the production of surface B–OH groups. Aluminum trichloride vapor reacts with both the single and hydrogen-bonded surface hydroxyls. On hydrolysis the single SiOH hydroxyls are again regenerated. There is, however, no evidence in the infrared spectrum for the existence of Al–OH groups on the surface of the hydrolyzed solid. Aluminum trimethyl also reacts with all the available surface hydroxyls and in some cases with surface siloxane linkages. In agreement with previous work, the results support a thesis that this reaction occurs in two stages. The first corresponds to reaction of aluminum trimethyl vapor with the surface hydroxyls producing $Si\text{–}O\text{–}Al\text{–}Me_2$ and  $Si\text{—}O\text{—}\overset{\overset{\displaystyle Me}{|}}{Al}\text{—}O\text{—}Si$ species at the surface, while the second corresponds to a further reaction of these species with neighboring surface Si–O–Si linkages resulting in the presence of both SiMe and AlMe groups on the ultimate surface. The changes in the infrared spectrum of the $AlMe_3$-treated silicas on exposure to excess water vapor are explained in terms of the relative hydrolytic stability of the Al–Me and $Si\text{–}CH_3$ surface species. Once again there is no clear evidence from the infrared spectrum of the hydrolyzed solid to suggest the presence of surface Al–OH species.

INTRODUCTION

In our earlier studies on the $SiO_2/BCl_3/H_2O$ system (*1*), we noted the formation of stable B–OH surface groups. From these studies, it became apparent that the reaction of hydroxylated silicas with the vapors of those metalloid and transition metal compounds which were hydrogen sequestering agents could perhaps be utilized to produce catalysts in which the catalytically active centers would exist at the surface of the silica support in a discrete array and possibly with a determinable structure and coordination.

In general it has long been known that compounds of the general type described above will react with the surface hydroxyls of silicas (*2*) and such reactions have often been used to measure the concentrations of the different types of surface hydroxyls which are known to exist on silicas (*2*, *3*). In terms of the present work, our spectroscopic studies of the $SiO_2/BCl_3/H_2O$ system have already been published (*1*). Peri (*4*) has published an account of his infrared investigations of the $SiO_2/AlCl_3/H_2O$ system and, just after our own investigations on the $SiO_2/AlMe_3/H_2O$ system were complete, Yates and his co-workers (*2*) published an extensive account of their spectroscopic studies on this same reaction. Comparing our results on $SiO_2/AlCl_3/H_2O$ with those of Peri (*4*), there are some minor differences but in the main the agreement is such that we do not include in the present text a detailed account of our own infrared work. For the $SiO_2/AlMe_3/H_2O$ case, although there is agreement in some respects with the work of Yates *et al.* (*2*), there are also some major differences. We find from our infrared studies that $AlMe_3$ reacts completely with both the single and hydrogen-bonded surface hydroxyls whereas Yates *et al.* (*2*) report a more selective attack of this compound on the single surface groups. Further, our thermogravimetric data show that the $AlMe_3$ attacks some of the Si–O–Si linkages on the dehydroxylated regions of the surface. This, together with our ESR studies on the production of CH_3 radicals by the reaction of oxygen gas with the $AlMe_3$-treated silicas (*5*), provides results additional to those previously reported. In view of this, and also noting with Yates *et al.* (*2*) the surprising absence in the literature of any account of other spectroscopic studies of the $SiO_2/AlMe_3/H_2O$ system, we present our results on this system in some detail.

EXPERIMENTAL METHODS AND MATERIALS

The Silicas

The silica powders and self-supporting discs prepared from them (ca. 30 mg cm^2) used in the present work have been examined previously by means of the techniques of gas adsorption (*6*), infrared spectroscopy (*7*) and chemical reactions of their surface hydroxyls with a range of chlorine-containing hydrogen sequestering agents (*3*, *8*). Overall, the results show that the silicas, which are all derived from an Aerosil sample, correspond to wide pore gels.* (R.A.3/5 also contains a small volume of pores of molecular dimensions). The hydroxylation of R.A.3/5 is such that after evacuation at ambient temperatures it carries 1.3 ± 0.1 single OH groups per 100 $Å^2$ of surface (type *A* sites), 3.2 ± 0.2 hydrogen bonded or paired hydroxyls per 100 $Å^2$ of surface (1.6 type *B* sites) and a concentration of "unavailable" hydroxyls within the bulk of the silica particles equivalent to a surface concentration of about 2.0 ± 0.2 per 100 $Å^2$. Annealing such discs in air at 700°C for 48 hr leads to R.A.3/5/700 which carries only single surface hydroxyls at a concentration of about 1.2 per 100 $Å^2$. The annealing also eliminates the microporosity and affects the bulk structure of the silica in such a way (*7*) that rehydroxylation of the disc in liquid water (at room temperature or 95°C) leads to very little regeneration of the bulk hydroxyls. Thus R.R.A.3/5/700 after evacuation at ambient temperatures carries virtually only surface hydroxyls in the form of 1.3 ± 0.1 type *A* sites and 1.6 ± 0.1 type *B* sites per 100 $Å^2$ of surface (*8*). It is pertinent to note here that it was necessary to anneal the discs themselves at 700°C since pressing hydroxylated silicas, annealed or otherwise, into self-supporting discs creates "bulk" hydroxyls in the disc (*7*).

The physical properties of the samples used in the present work are shown in Table 1 (*7*, *8*).

Infrared Studies

The basic experimental procedures were the same as those described previously for the $SiO_2/BCl_3/H_2O$ system (*1*). $AlMe_3$ (K & K Laboratories Limited) was transferred as the liquid into glass ampoules sealed with greaseless stopcocks. The ampoules were sealed to the appropriate vacuum manifold and the liquid was distilled as required. Analytical grade $AlCl_3$ (ex B.D.H.) was transferred to Pyrex glass ampoules sealed with break seals. These ampoules were then blown onto a vacuum manifold and the seals were broken as required for sublimation and sample treatment. The D_2O used for the isotopic exchange experiments was 99.7% pure (ex Norsk Hydro).

For the $AlMe_3$ studies the cell used was that described by Armistead *et al.* (*9*). For the $AlCl_3$ an optically clear, OH free silica tube of 20-mm i.d. was connected by a

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* See Refs. (*6* and *7*) for a detailed account of the sample nomenclature.

TABLE 1

Sample	BET N_2 area (m^2 g^{-1})	Surface hydroxylation (sites/100 $Å^2$)		Bulk hydroxyls (equivalent to a surface conc of x/100 $Å^2$)
		Type A	Type B	
R.A. 3/5 [i.e., R.A. 3 pressed at 5 tons cm^{-2} (*8*)]	168 ± 3	1.3 ± 0.1	1.6 ± 0.1	$x = 2.0 + 0.2$
R.A. 3/5/700	144 ± 3	1.2 ± 0.1	—	—
R.R.A. 3/5/700	144 ± 3	1.3 ± 0.1	1.6 ± 0.1	$x \approx 0.1 - 0.2$

graded seal to a Pyrex manifold. The spectra were recorded with the silica discs held in a platinum cradle in the silica portion of this device which could be heated as appropriate by furnaces and electrical heating tapes for sublimation of the $AlCl_3$ sample. All the spectra were recorded on a Perkin-Elmer 125 grating infrared spectrophotometer using a spectral slit width of 3 cm^{-1} or less. The spectrometer was continually flushed with dry air during the recording of spectra.

Thermogravimetric Studies

Silica discs were hung by a glass fiber on a thermostated (25°C) McBain quartz spring balance (sensitivity, 45.5 cm g^{-1}). The sample treatments were identical to those used in the infrared studies (see figure legends).

Mass Spectrometric Studies

Qualitative analyses of the composition of the vapor phase during the reactions of the silicas with $AlMe_3$ were carried out by means of an A.E.I. M.S.10 mass spectrometer using a direct inlet capillary sampling system (*10*). Previous experience had shown us that the mass spectrometer was incompatible with vapors such as BCl_3 and $AlCl_3$, and mass spectrometric analyses were not carried out on the BCl_3/SiO_2 and $AlCl_3/SiO_2$ systems. In these latter cases it is fortunate that the reactions are amenable to analysis by the appropriate "wet" volumetric methods (*9*).

RESULTS AND DISCUSSION

$SiO_2/BCl_3/H_2O$

When hydroxylated silicas are reacted with excess BCl_3 vapor at room temperature, the surface hydroxyls react quickly and completely (*7*). Spectrum 1 of Fig. 1 shows only an asymmetric absorption band centered around 3650 cm^{-1}, which corresponds to the bulk hydroxyls present in this unannealed sample. The single (*A* sites) and the interacting (*B* sites) surface hydroxyls have been removed by the BCl_3 and so their corresponding absorption bands at 3750

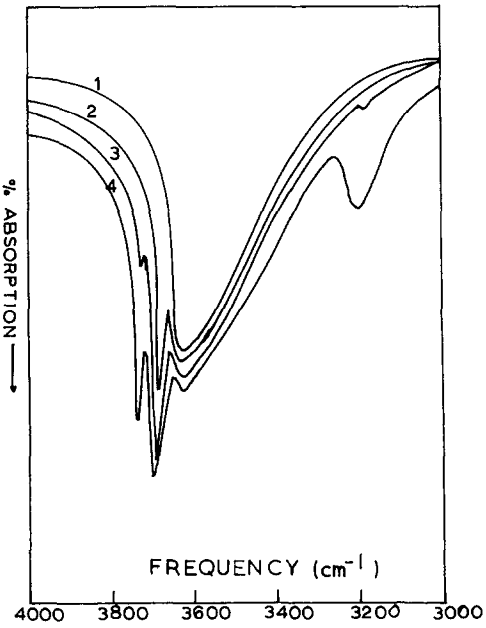
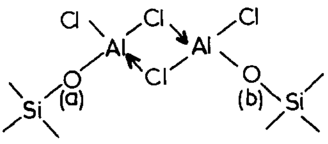


FIG. 1. All the spectra presented in the paper were recorded with the sample at ambient temperature (≈30–35°C). (1) R.A.2/5 after treatment with excess BCl_3 at room temperature, followed by evacuation at room temperature; (2, 3, and 4) after consecutive additions of small quantities of H_2O vapor to the sample corresponding to spectrum (1)—with evacuation at room temperature between each dose. [R.A.2/5 and R.A.3/5 are similar preparations, see Ref. (*7*) for a detailed comparison.]

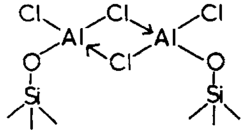
cm^{-1} (sharp) and 3550 cm^{-1} (broad) are not present. When the sample corresponding to spectrum 1 is treated successively with doses of water vapor, each of which in themselves are too small in quantity to effect complete hydrolysis, the spectra resulting correspond to 2, 3, and 4 in Fig. 1. The sharp band at 3695 cm^{-1} which appears on hydrolysis is due to the creation of stable B–OH surface groups (*7*, *11*). Further work on this system (*10*) shows that the same final surface state may be achieved by the addition of an immediate excess of water to the BCl_3 treated silica giving a surface carrying type A silanols and B–OH groups.

$SiO_2/AlCl_3/H_2O$

$AlCl_3$ is a solid at ambient temperatures and it was necessary to react the silicas with this vapor at about 200°C. $AlCl_3$ is largely dimeric under solid–gas equilibrium conditions at low temperatures but the heat of dimer dissociation (<15 kcal $mole^{-1}$) is sufficiently small for the treatment and prolonged evacuation of the silicas at 200°C (see figure legends) to be sufficient to remove any excess $AlCl_3$ held at the reacted surface by coordinate bonding involving chlorine atom lone pair electron donation to aluminum. The possibility of Al_2Cl_6 reacting with the type *B* sites to give surface structures of the type below can be excluded on

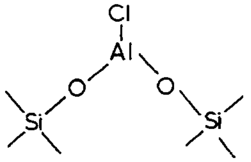


stereochemical grounds (*1*, *8*) as the $O_{(a)}$–$O_{(b)}$ distance has to be sufficiently small for monomeric BCl_3 to form an unstrained hydrolytically stable (SiO_2) B–OH species of the type discussed above (*7*). At type *A* surface sites where the O–O distance of neighboring hydroxyls is thought to be of the order of 5 Å, with the Si–O bond of the surface hydroxyl perpendicular to the surface (*8*), it seems quite possible that structures of the following type may exist after reaction of the silica with $AlCl_3$.

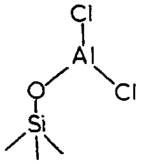


In the overall context of this reaction, it is worth noting that Boehm *et al.* (*13*) showed that the reactions of BCl_3 and $AlCl_3$ with hydroxylated silicas exhibited comparable stoichiometries under experimental conditions similar to those used in the present work. We therefore conclude* that, as in the BCl_3 case, reaction of a "fully" hydroxylated silica carries aluminum atoms bonded as shown below:

From *B* sites (*8*)



From *A* sites (*8*)



The spectra shown in Figs. 2 and 3 illustrate the complete removal of the surface OH species by $AlCl_3$ under the conditions described. They also demonstrate a more surprising result; on hydrolysis of the $AlCl_3$-reacted silicas there is no evidence for the formation of an Al–OH surface species, although the type A silanols are regenerated. Even partial hydrolysis of the $AlCl_3$-treated surface failed to produce an absorption band in the spectrum analogous to that present in the $SiO_2/BCl_3/H_2O$ system. This result is in accord with those reported by Peri (*4*) on the $SiO_2/AlCl_3/H_2O$ system.

$SiO_2/AlMe_3/H_2O$

The "fully" hydroxylated silicas [R.A. 3/5 and R.R.A. 3/5/700]. Like $AlCl_3$, $AlMe_3$ vapor is largely dimeric at ambient temperatures at its equilibrium vapor pressure. However, the evacuation conditions of the silicas treated with $AlMe_3$ were such that the same considerations may be expected to apply to the surface structure of reacted and evacuated $AlMe_3$-treated silicas as those described above for the $SiO_2/AlCl_3$ system.

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* The reader is referred to Ref. (*8*) for a detailed discussion of this particular point.

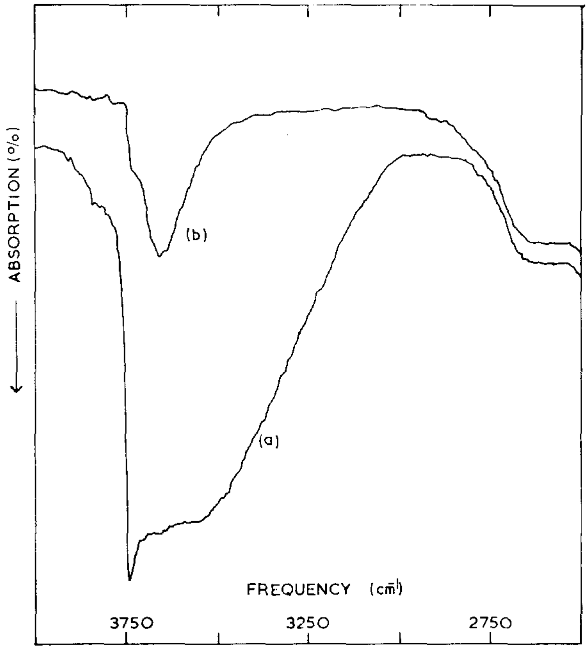


FIG. 2. Spectrum of R.R.A.3/5/700 after evacuation at room temperature; (b) sample as above evacuated at 200°C, reacted with excess $AlCl_3$ vapor and evacuated at 200°C.

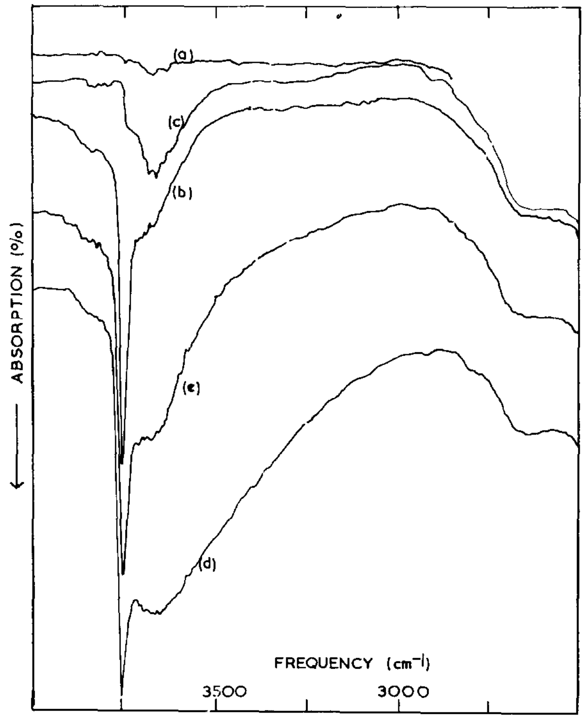


FIG. 3. Spectrum of empty silica cell; (b) R.A.3/5/700 after evacuation at 500°C; (c) sample as for (b) reacted with excess $AlCl_3$ vapor at 200°C and then evacuated at 200°C; (d) sample as for (c) hydrolyzed with excess H_2O at room temperature and then evacuated at 200°C; (e) sample as for (d) evacuated at 400°C.

As discussed below, the thermogravimetric and infrared data indicate that the evacuation conditions used do in fact remove physisorbed AlMe$_3$, which would presumably be bonded to the modified surface by relatively weak methyl bridges.

Spectrum 1 of Fig. 4 corresponds to an unannealed pressed disc of "fully" hydroxylated silica. Treatment with excess AlMe$_3$ vapor markedly alters the OH region of the spectrum. The sharp band at 3750 cm^{-1} has disappeared and the absorption intensity around 3550 cm^{-1} is also greatly diminished. The use of such unannealed discs to establish the reactivity of the surface hydroxyls towards AlMe$_3$ is complicated by the large residual asymmetric absorption band at 3650 cm^{-1} that corresponds to the large concentration of bulk hydroxyls in this specimen. That this 3650 cm^{-1} band is caused by bulk rather than surface hydroxyls is illustrated by the spectra shown in Fig. 5, which correspond to the AlMe$_3$-treated disc after exposure to consecutive small doses of D$_2$O vapor, when it can be seen that the 3650 cm^{-1} band intensity remains virtually constant.

In order to circumvent this complication concerning the reactivity of the surface hydroxyls we present in the remaining spectra the results obtained with annealed discs in which the 3650 cm^{-1} band makes only a minor contribution to the spectrum in accord with the reasons given elsewhere (7). In Fig. 5, the deuterium exchanged disc (spectrum b) shows bands at 2620 cm^{-1} (OH $\equiv$ 3550 cm^{-1}) and at 2755 cm^{-1} (OH $\equiv$ 3750 cm^{-1}) corresponding to the type *B* and type *A* surface hydroxyl sites, respectively. Reaction of the deuterated specimen with AlMe$_3$ as before leads to the disappearance of both absorption bands (spectrum c). Since deuterium exchange produces no change in absorption intensity in the 1640 cm^{-1} region of the spectrum it is clear that the 2620 cm^{-1} (3550 cm^{-1}) absorption band corresponds to surface hydroxyls rather than adsorbed molecular water. We therefore

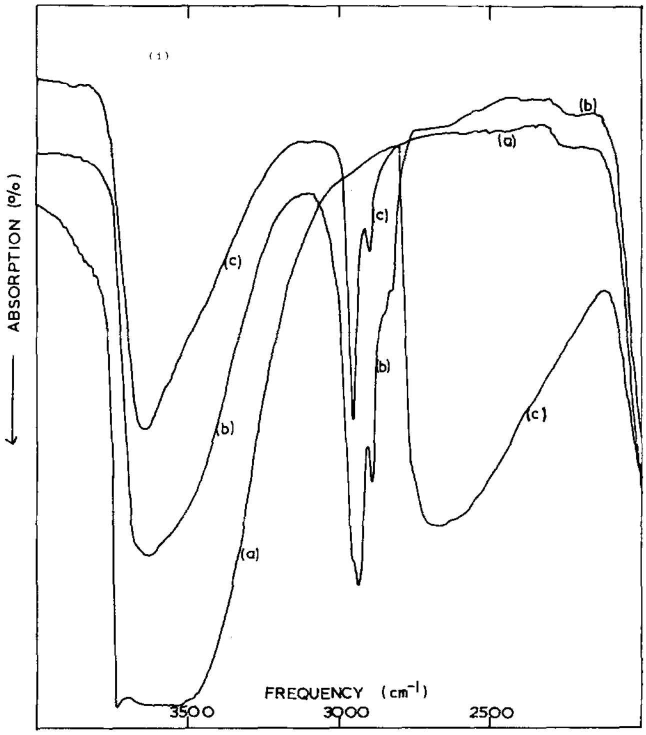


FIG. 4i. (a) R.A.3/5 after evacuation at room temperature; (b) sample as for (a), exposed to excess AlMe$_3$ vapor at room temperature and then evacuated at room temperature; (c) see legends of Fig. 4ii.

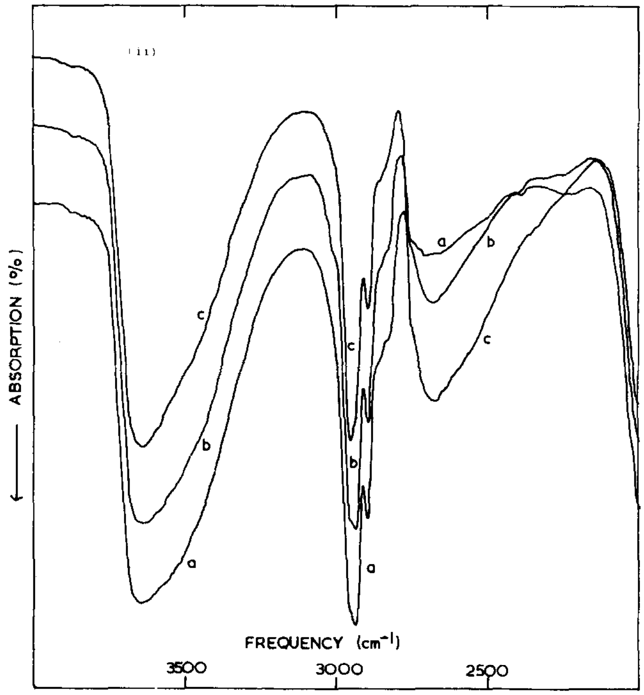


FIG. 4ii. (a, b, and c) Sample as for Fig. 4i (b), exposed to successive small quantities of D_2O at room temperature and evacuated after each dose. The sample was then exposed to a large excess of D_2O vapor at room temperature and evacuated at room temperature. The corresponding spectrum is Fig. 4i (c), which is placed-to render an easier comparison with spectrum (b) of Fig. 4i.

conclude from these experiments that under the experimental conditions described, which are closely similar to those used by Yates *et al.* (*2*), $AlMe_3$ does not react selectively with the surface hydroxyls.

Turning now to the fundamental C–H absorption region of the spectra shown in Figs. 4 onwards, we see that in all cases the spectra of the $AlMe_3$-reacted silicas exhibit four C–H absorption bands; at 2958, 2938, 2897, and 2830 cm^{-1}. Hydrolysis with D_2O or H_2O vapor, either by consecutive small doses or with an immediate excess, simplifies the spectrum and the hydrolyzed surface exhibits only two bands in the C–H spectrum at 2958 and 2905 cm^{-1}. This result suggests that the $AlMe_3$-reacted silicas carry two types of methyl group; namely those that are susceptible to hydrolysis and those which are not.

Mass spectrometric analyses of the gas phase products of these reactions showed that when the silicas were reacted with $AlMe_3$ only methane was left in the gas phase after condensation of the excess $AlMe_3$ at $-78°C$. Similarly, only methane was observed when H_2O was admitted to the outgassed $AlMe_3$ treated surfaces. The quantity of methane evolved on reaction of a silica sample with $AlMe_3$ was of a comparable magnitude to the quantity of methane evolved on subsequent hydrolysis of the outgassed solid product.

These mass spectrometric results are important since, were all the methyl groups remaining on the surface joined to silicon atoms as suggested by Yates *et al.* (*2*), then one would expect no liberation of methane on admitting water to the outgassed $AlMe_3$ reacted samples. In comparing our results in general with those of Yates and his coworkers (*2*) on this point we note that their experimental technique included the outgassing of the $AlMe_3$-treated silicas at 400°C prior to admitting H_2O vapor to the system. Figure 6 shows the spectra corresponding to such a treatment and demonstrates that the hydrolyzable methyl groups are removed

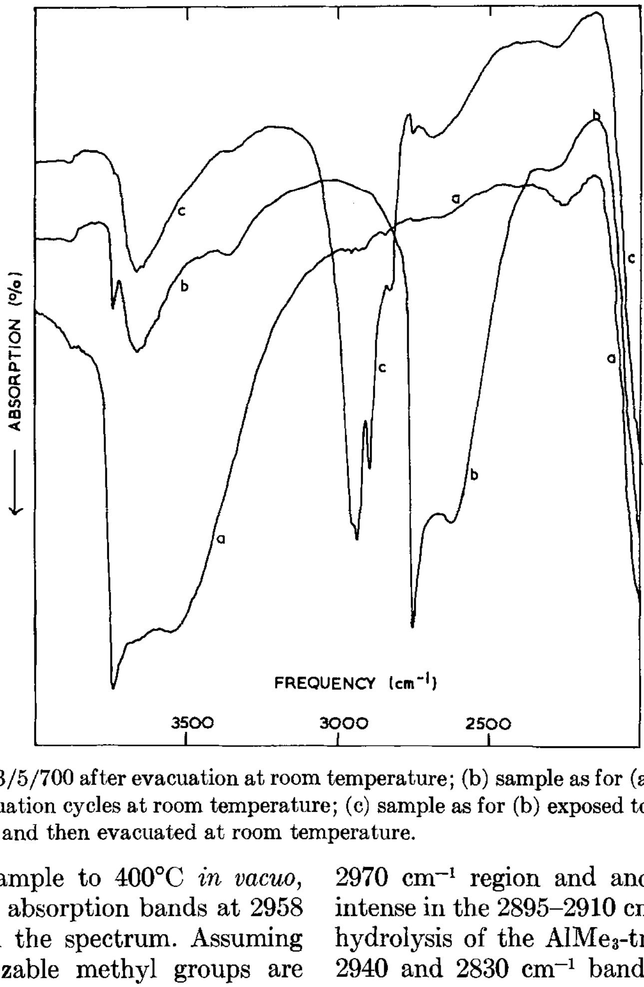


FIG. 5. (a) R.R.A.3/5/700 after evacuation at room temperature; (b) sample as for (a), after five consecutive D_2O vapor/evacuation cycles at room temperature; (c) sample as for (b) exposed to excess $AlMe_3$ vapor at room temperature and then evacuated at room temperature.

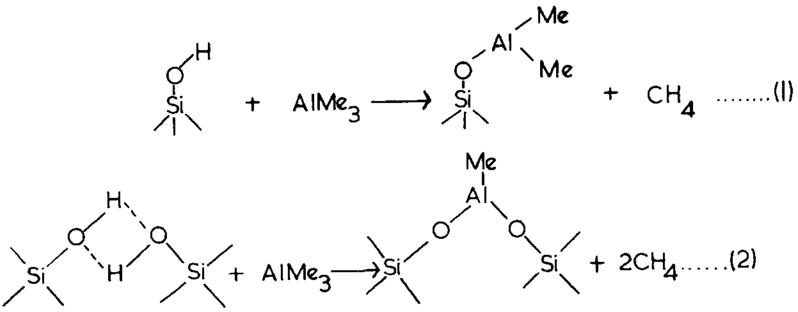
by heating the sample to 400°C *in vacuo*, leaving only C–H absorption bands at 2958 and 2905 cm^{-1} in the spectrum. Assuming that the hydrolyzable methyl groups are bonded to aluminum atoms in the surface, their thermal elimination is not surprising, since it is known that the $Al–CH_3$ bond is thermally unstable to a degree such that $AlMe_3$ itself undergoes thermal decomposition at a measurable rate at temperatures as low as 300°C (*14*). (The samples outgassed at 400°C after the $AlMe_3$ reaction were black in color indicating that decomposition with carbonization had occurred, whereas similar samples heated in the presence of excess water vapor remained colorless at temperatures up to 500°C.)

In assigning the C–H bands in the spectra of the $AlMe_3$-treated silicas we first note that $AlMe_3$ exhibits three absorption bands at 2940, 2875 and 2830 cm^{-1} and that the spectra of compounds containing methyl groups bonded to silicon atoms exhibit two C–H absorption bands, one in the 2960–2970 cm^{-1} region and another that is less intense in the 2895–2910 cm^{-1} region (*2*). On hydrolysis of the $AlMe_3$-treated silicas, the 2940 and 2830 cm^{-1} bands disappear from the spectrum and the 2895 cm^{-1} band is reduced in intensity, leaving only those two bands at 2960 and 2905 cm^{-1} characteristic of Si–Me groups (Figs. 4–7). Considering the mass spectrometric and infrared results together we conclude that the outgassed $AlMe_3$-treated silicas carry some methyl groups joined to aluminum atoms, which may be removed by hydrolysis at ambient temperatures, and some methyl groups joined to surface silicon atoms which are hydrolytically stable under similar conditions.

The thermogravimetric experiments on the "fully" hydroxylated silica discs indicated that the reaction between the surface hydroxyls and the $AlMe_3$ proceeded in accord with the reactions:

For type *A* sites (1.3 ± 0.1 per 100 Å^2)
For type *B* sites

All the weight changes observed were in



accord with this stoichiometry to within 5%. Furthermore, there was no detectable weight change on raising the outgassing temperature of the AlMe$_3$-treated silicas from ambient to 100°C. This supports the assertion made earlier that prolonged evacuation of the reacted discs at room temperature removes any physisorbed AlMe$_3$ from the surface.

Reactions (1) and (2), however, can only represent the initial stages of the AlMe$_3$/SiO$_2$ reaction, since the infrared data show that secondary reactions occur which lead to the formation of surface Si–Me groups, presumably by reactions of the type as suggested by Yates *et al.* (*2*).

Surface "rearrangements" of this type produce no weight change of the sample but a very careful analytical study of the ratio of the methane liberated during hydrolysis to that liberated during the initial reaction of the AlMe$_3$ with the silicas may provide information as to the relative predominance of type (3) reactions.

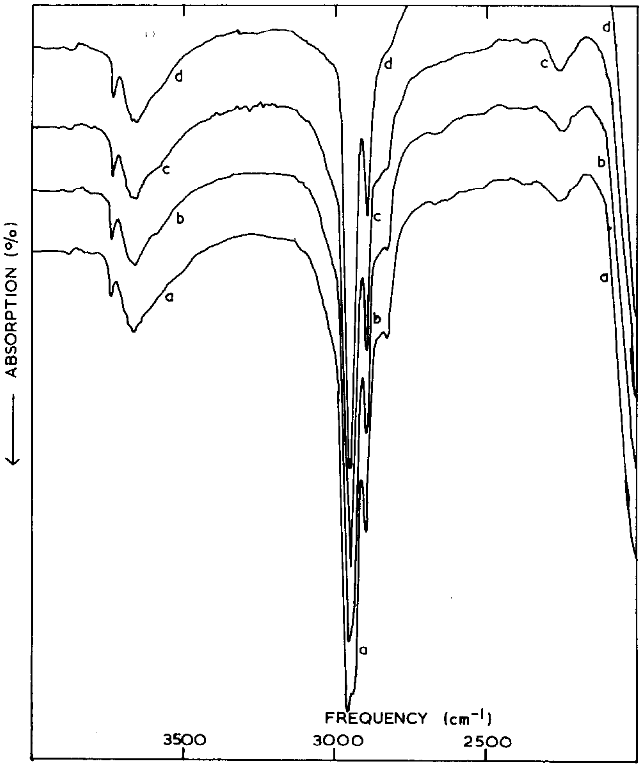


FIG. 6i. (a) R.A.3/5/700 after exposure to excess AlMe$_3$ vapor at room temperature and then evacuated at 150°C for 30 min; (b) sample as for (a), evacuated at 250°C for 30 min; (c) sample as for (b), evacuated at 350°C for 30 min; (d) sample as for (c), evacuated at 400°C for 30 min.

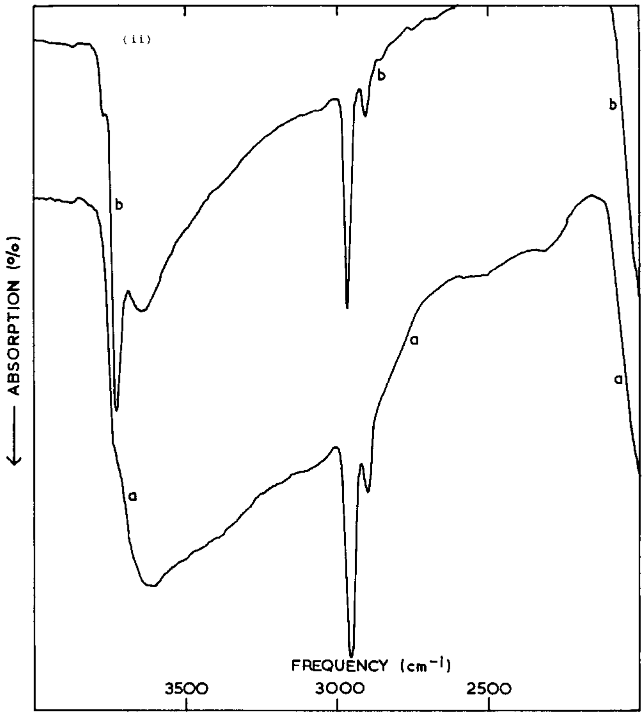
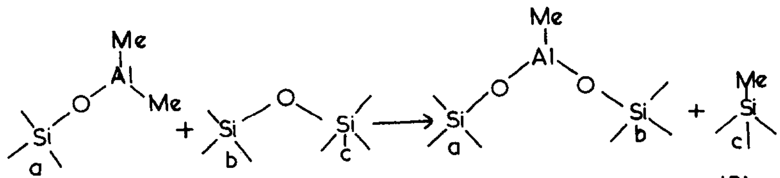


FIG. 6ii. (a) Sample as for Fig. 6i (d), after exposure to excess H_2O vapor and then evacuated at room temperature; (b) sample as for (a) evacuated at 250°C for 90 min.

The reaction of $AlMe_3$ with silicas carrying only single surface hydroxyls (R.A. 3/5/700). The infrared spectra corresponding to these experiments are shown in Figs. 6 and 7. The essential features are similar to those shown in the spectra corresponding to reaction with the "fully" hydroxylated discs. All the surface hydroxyls react. The C–H spectrum again exhibits four absorption bands after the $AlMe_3$ reaction and then two after the subsequent hydrolysis of the ambiently evacuated samples. The mass spectrometric data again show that comparable quantities of CH_4 are the only gas phase products volatile at $-78°C$, both after the initial reaction and the subsequent hydrolysis as before. We therefore suggest that the single hydroxyls on these partially dehydroxylated silicas follow the reaction scheme indicated by Reaction (1) with a possible subsequent rearrangement according to Reaction (3).

However, the thermogravimetric studies on these singly hydroxylated discs produced a surprising result. The weight increases observed were always far in excess (≈ 70–100%) of that to be expected with only Reaction (1) occurring at the type *A* sites. This "excess" weight increase could be caused by physisorbed $AlMe_3$ remaining at the surface after ambient evacuation, but further outgassing at temperatures up to 120°C caused no weight decrease and so this hypothesis seems unlikely. Our ex-



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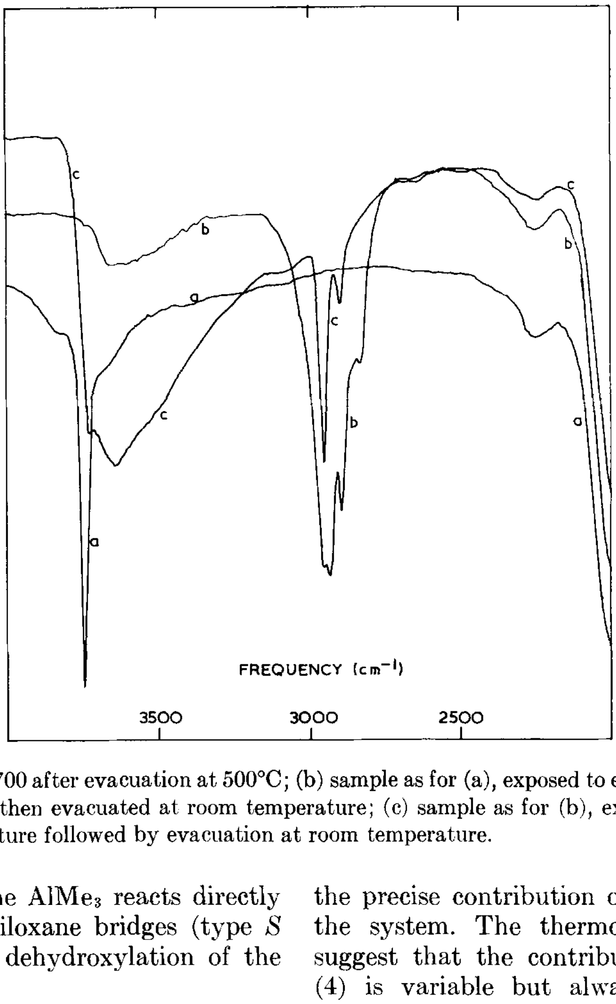
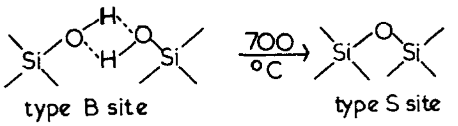


FIG. 7. (a) R.A.3/5/700 after evacuation at 500°C; (b) sample as for (a), exposed to excess $AlMe_3$ vapor at room temperature and then evacuated at room temperature; (c) sample as for (b), exposed to excess H_2O vapor at room temperature followed by evacuation at room temperature.

planation is that the $AlMe_3$ reacts directly with the strained siloxane bridges (type *S* sites) produced by dehydroxylation of the type *B* sites, i.e.,



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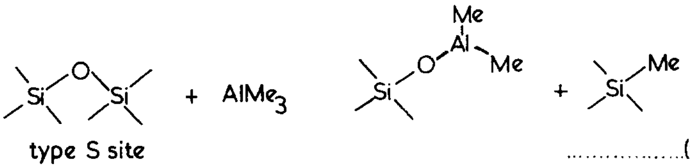

................(5)

The species (c) could then possibly further react with surface oxygen atoms as in Reaction (3). Again it seems possible that analytical determinations of the CH_4 evolved during the initial $AlMe_3$ reaction and subsequent hydrolysis steps would establish the precise contribution of Reaction (5) to the system. The thermogravimetric data suggest that the contribution of Reaction (4) is variable but always occurs to an extent within the limits of 1.2–1.6 type *S* sites/100 A^2 of surface.

CONCLUSIONS

For the $AlMe_3/SiO_2$ system our results are in accord in part with those of Yates *et al.* (*2*) in so far as we too find evidence for surface rearrangement reactions giving rise to $SiCH_3$ groups. Unlike Yates and his co-workers (*2*), however, we believe that our results indicate that there are AlMe groups also present on the reacted silicas. We are also convinced that both the single and hydrogen-bonded hydroxyls react with $AlMe_3$ with an apparently equal facility.

There are two final points: Firstly, none of the hydrolyzed discs from the $AlMe_3$ or $AlCl_3$-reacted silicas showed any absorption bands that could be attributed to Al–OH species of a type analogous to the B–OH species produced by hydrolysis of the BCl_3 treated materials, except possibly those samples reacted at room temperature with $AlMe_3$ and then heated in water vapor (15 mm Hg pressure) at about 200–250°C, followed by evacuation at 200–250°C. Under those conditions a shoulder at about 3780 cm^{-1} [see spectrum (b) of Fig. 6ii] was observed in the corresponding infrared spectrum. However, removal of this band from the spectrum by heating the solid to 300°C makes it seem unlikely that it corresponds to Al–OH. Secondly, as reported by Peglar *et al.* (*5*), although hydrolysis of the $AlMe_3$-treated silicas apparently destroyed all the Al–Me groups in the samples, subsequent exposure of the hydrolyzed discs to air or dry oxygen produced methyl radicals trapped at the solid surface. No infrared spectroscopic change was detected during this oxidation. Since the nonreactivity of the $SiCH_3$ function towards oxygen under such conditions is well established, this result was somewhat unexpected.

Finally, in the context of the surface modification of silicas, it is normally assumed that the modifying reagent reacts solely with the surface hydroxyls. With $AlMe_3$, apparently the strained siloxane bridges (type *S* sites) are also surface reaction sites. It follows that under more stringent reaction conditions (e.g., reaction at 400°C) other reagents such as $AlCl_3$, BCl_3, $SiMe_xCl_{(4-x)}$ may also react with these type *S* sites.

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