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AN INFRARED STUDY OF THE REACTION OF METHANOL WITH SILICEOUS SURFACES

By

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Abstract

Infrared Spectra were recorded of the reactions of methanol with the surfaces of porous glass as well as silica and boria-impregnated silica. Several reaction occur with porous glass. Methanol is hydrogen-bonded to surface SiOH and B-OH groups. Si-OCH_3 groups are formed at 30° predominantly through reaction strained siloxane bridges; at higher temperatures there is an esterification reaction with SiOH groups. B-OCH_3 groups are formed via both mechanisms. B-OCH_3 groups decompose above 200° and $SiOCH_3$ groups are formed. The mechanism for this involves the migration of methyl radicals from boria islands to the silica portion of the glass. Near 600° some Si-OCH_3 groups decompose and B-OH groups are formed.

The adsorption of methanol on silica and porous glass surfaces has been the subject of several studies, with somewhat divergent results.[1~7] Two mechanisms were proposed for the surface methylation reaction. However, recent work with porous glass and silica surfaces showed that the reactivity of the silica skeleton could be affected by impurities on the surface.[8~15] As the chemical modification of siliceous surfaces was of interest to us, and the results of further work might contribute to our knowledge of surface methylation, we began a comprehensive study of the reaction of methanol with porous glass and silica surfaces, using infrared techniques.

Experimental

Most of the experimental procedures have been described elsewhere.[9~15] Corning Code 7930 porous glass was purchased from Corning Glass Works in the form of 1 mm-thick sheets. Samples approx. 10×25 mm were cut from the sheet. Some porous glass specimens were reduced in thickness to

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approx. 0.1 mm by grinding, in order to permit the recording of spectra below 2000 cm^{-1}. Although such "thin" plates plates permitted the 2000–1400 cm^{-1} region to be examined, the transmittance is that region was low and the bands observed were quite weak. Consequently, most of the work with porous glass was carried out with 1 mm-thick specimens.

The pure silica chosen for the work was Cab–O–Sil.[16] Some experiments were also carried out with Cab–O–Sil impregnated with boria by means of the well-known incipient wetness method. About 40–50 mg of the dry powders were compressed at 640 kg/cm^2 to form self-sustaining pellets of approx. 2 cm diameter. The methanol used was spectro quality grade, distilled several times under reduced pressure.

Spectra were recorded with Perkin-Elmer Models 521 or 621 spectrophotometers fitted with Reeder thermocouples. All spectra were measured with the samples at room temperature. A second infrared cell was placed in the reference beam of the spectrophotomeier to compensate for absorptions due to gaseous methanol and the ambient atmosphere.

Results and Discussion

Silica

Series of infrared spectra were recorded of methanol sorption and reaction with Cab–O–Sil samples under a variety of experimental conditions such as degassing temperature, sorption temperature and time, and desorption. Some typical spectra are shown in Figs. 1 and 2, to permit comparison with spectra of porous glass to be discussed later. Most of the spectra of Cab–O–Sil need not be considered, in view of the recent papers on methanol adsorption on Aerosil silica by BORELLO *et al.*[17] Their work, with which our data on Cab–O–Sil and mechanisms are in general agreemet, leads to the following band assignments. Bands at 2845 and 2950c m^{-1} are respectively due to the symmetric and asymmetric CH_3 streching vibration of physically adsorbed methanol. Bands at 2855 and 2959 cm^{-1} are respectively due to the symmetric and asymmetric CH_3 stretching vibrations of methanol dissociatively chemisorbed to form $\equiv Si–O–CH_3$; these bands are shown particularly well in spectrum F of Fig. 1. A band and shoulder near 3000 and 2920 cm^{-1} are attributed to overtones of the CH_3 bending modes probably in Fermi resonance with the stretching modes.[18,19] A band at 3620 cm^{-1}, *e.g.* spectrum B, Fig. 2, is attributed to the relatively unperturbed O–H stretching fundamental of physically adsorbed methanol. A hydrogen-bonded structure I leads to a broad absorption

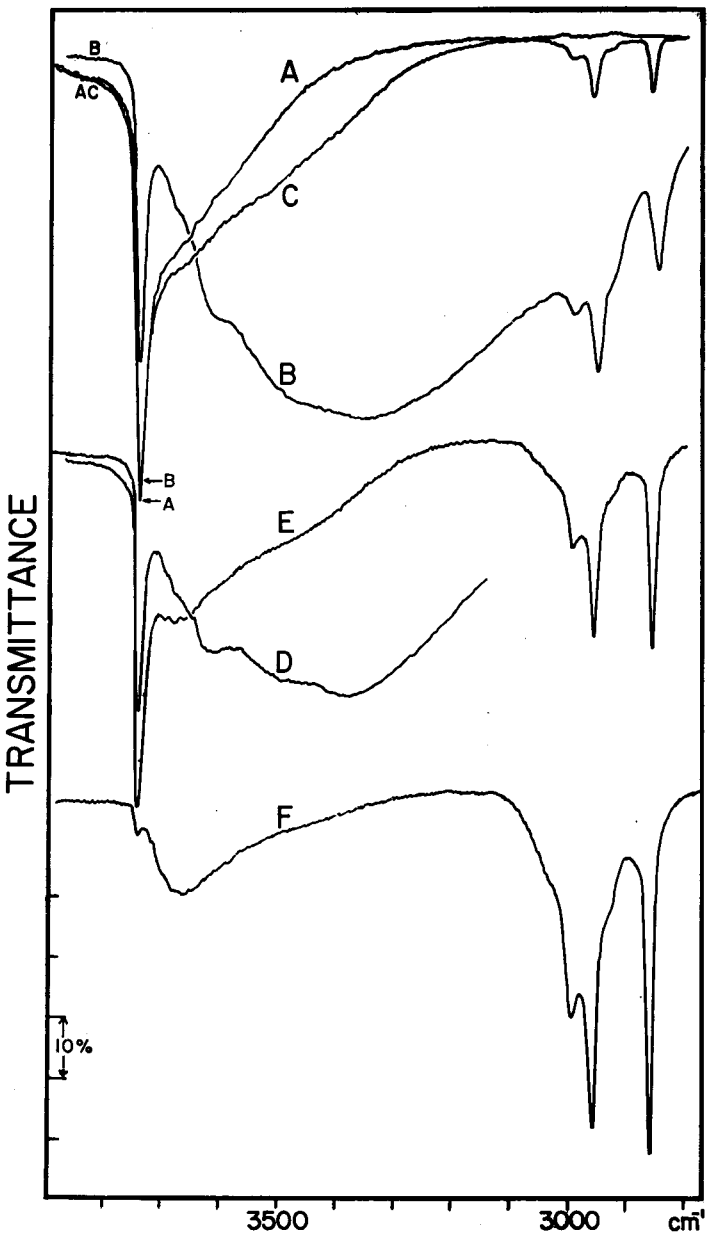


Fig. 1. Methanol sorption on silica

A: "background" spectrum of pure Cab-O-Sil silica, after degassing for 10 hrs at 400°. B: after exposure to 20 Torr methanol at 30°. C: after degassing for 1 hr at 30°. D: after heating in 20 Torr methanol at 400° for 2 hrs and cooling to 30°. E: after degassing for 2 hrs at 30°. F: after heating in 20 Torr methanol at 400° for 40 hrs, and degassing for 1 hr at 400°.

The ordinates of spectra E, D, and of F, are displaced. The transmittance was 85% for each spectrum at 3900 cm^{-1}.

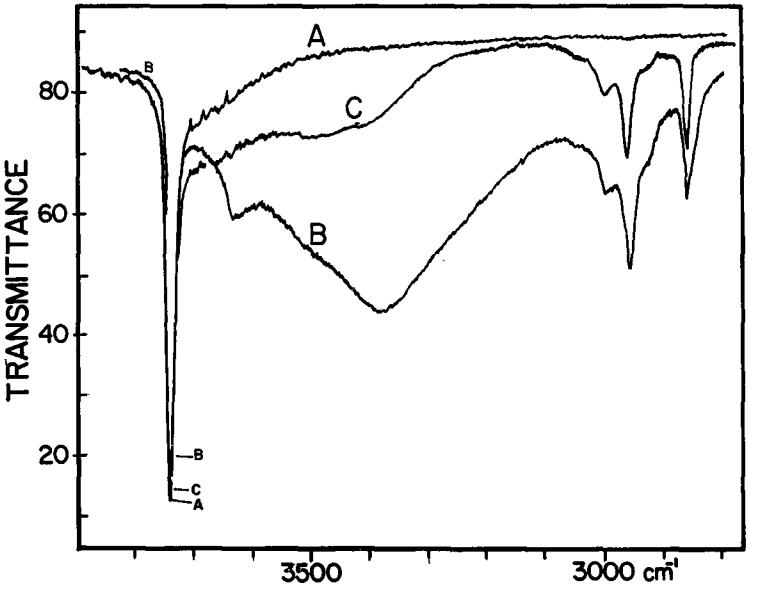
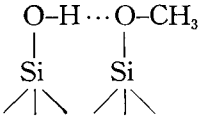


Fig. 2. Methanol sorption on silica

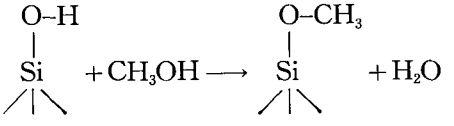
A: "background" spectrum of pure Cab-O-Sil silica after degassing for 10 hrs at 750°. B: after exposure to 20 Torr methanol at 30°. C: after degassing for 2 hrs at 30°.

Structure I



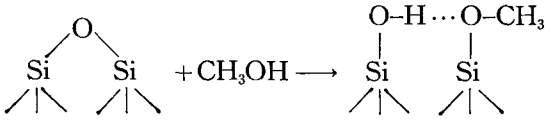
at 3500 cm^{-1}, *e.g.* spectrum D, Fig. 1. A second broad band near 3400 cm^{-1} is attributed to hydrogen bonding of adsorbed methanol to surface hydroxyls; examples are seen in spectrum D of Fig. 1 and spectrum B of Fig. 2. A variety of data, considered in detail elsewhere,[17] point to adsorption by means of single and multiple hydrogen bonds and adsorbate-adsorbate interaction.

It has been saggested that surface methylation occurs through the esterification of surface hydroxyls,[3,6]



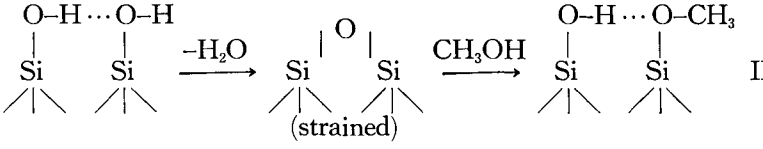
I

or through the reaction of methanol with siloxane bridges[1,7]



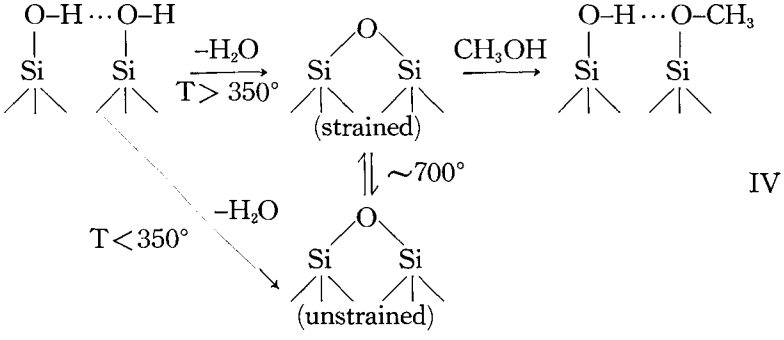
II

BORELLO *et al.* measured the number of chemisorbed methoxyls as a function of surface hydroxyls and found, in the temperature range of 400–700° used for activating the samples, that the proportionality coefficient of the two quantities was very close to 2, *i.e.* one methoxyl group formed for every 2 hydroxyl groups eliminated by outgassing. This suggested the reaction III, because not every siloxane bridge was active. However,



III

at interaction temperatures above 700°, the ratio (OH eliminated)/(OCH_3 formed) fell below the value of 2, indicating that some of the strained surface bridges were annealed into an unstrained configuration no longer reactive to methanol. The over-all mechanism can thus be written,



IV

The mechanisms described by BORELLO *et al.* very well explain the low temperature chemmisorption and physical adsorption on Aerosil and Cab–O–Sil, as well as some of the features of sorption on porous glass. We add the following observations.

Heating Cab–O–Sil in methanol vapor at various temperatures led to the gradual diminution of the 3648 cm^{-1} band of free hydroxyls. The methylation occurred slowly even with samples initially degassed at 300°, was noticeable at a reaction temperature of 100°, and certainly involved the esterification reaction I. After some methylation had occurred, a broad band near 3680–3660 cm^{-1} began to be noticeable, *e.g.* spectrum E, Fig. 1. The band became better de-

fined as the methylation cotinued, *e.g.* spectrum F, Fig. 1. However, prolonged treatments with methanol at 400° did not diminish the 3660 cm^{-1} band beyond the stage shown in spectrum F, Fig. 1. Also, the 3680 cm^{-1} band which was detected after severe methylation was smaller with samples which had been activated at high temperatures, *e.g.* spectrum A, Fig. 4, of a methylated specimen which had been activated at 800°. Such behavior indicates that the 3680 cm^{-1} band was brought about by species not accessible to methanol, *i.e.* "internal" hydroxyls. A similar band has been found to be unaffected by adsorption of dimethyl[19] and diethyl ether[19,21] and dietyl amine[20]; and DAVIDOV *et al.*,[22] in their studies on the reaction of chlorosilane with Aerosil silica,

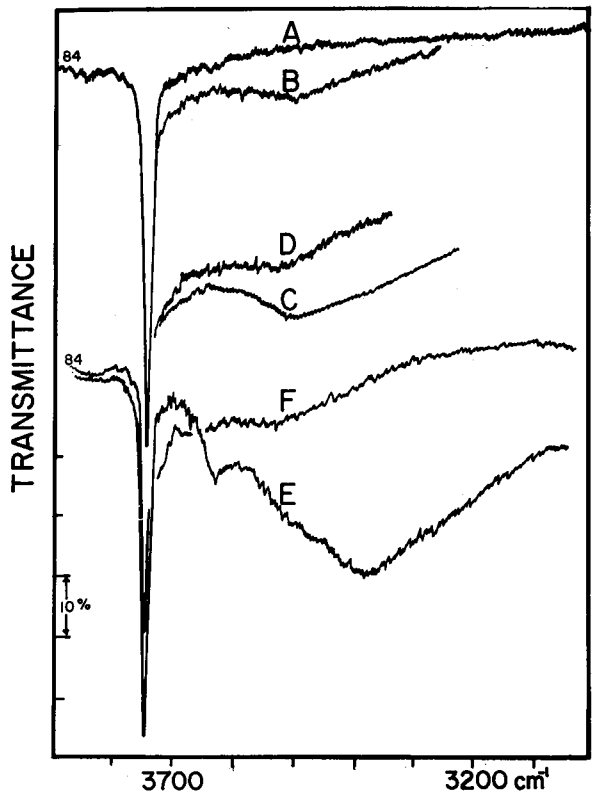


Fig. 3. Water sorption on silica

A: "background" spectrum of pure Cab-O-Sil after degassing for 10 hrs. at 800°. B: after exposure to 11 Torr H_2O at 30°. C: after exposure to 24 Torr H_2O at 30°. D: after degassing for 20 hrs at 30°. E: after exposure to 25 Torr methanol at 30°. F: after degassing for 30 min at 30°.

The ordinates of spectra C, D and of spectra, E, F are displaced. The transmittance was 84% at 3900 cm^{-1} for each trace. Only portions of spectra C and D are shown.

concluded that a band near 3650 cm^{-1} was caused by internal hydroxyls. The latter would not be important if unaccessible to the adsorbate. However, the broad 3680 cm^{-1} band would contribute to the intensities of bands in the O–H region, and could cause some uncertainty in measurements of the intensity of the free hydroxyl bands. Also, water sorption on Cab-O-Sil brings about a broad band near 3500 cm^{-1}. Some effects of water sorption are shown in Fig. 3. It is interesting to note that the spectrum of methanol sorbed on a sample initially activated at 800° but containing some sorbed water shows similar structure, *i.e.*, bands near 3500 and 3400 cm^{-1}, as spectra of methanol sorbed on samples activated at temperature below 700°. An absorption caused by water formed by reaction I could thus contribute to the total intensity of the 3500 cm^{-1} band which BORELLO *et al.* attributed to multiply-hydrogen-bonded, adsorbed methanol. Such results suggest that although the room temperature chemisorption would occur predominantly *via* mechanism IV as stressed by BORELLO *et al.*, there may be a small contribution to the surface methylation *via* the much slower mechanism I.

Some experiments were also made of methanol sorption of specimens methylated to various extents. In general, the spectra showed that increasing the degree of methylation, and consequently decreasing the surface hydroxyl concentration, decreased the amount of physically adsorbed methanol. An extreme case is shown in Fig. 4. The small free hydroxyl band of spectrum A shows that methylation was almost complete. When the specimen was exposed to methanol (spectrum B), the amount of methanol taken up was small. Such results indicate that hydrogen bonding of methanol to methoxyl groups is minimal.

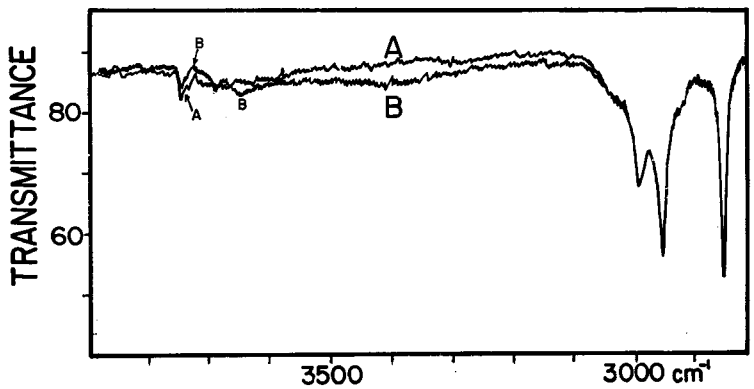


Fig. 4. Methanol sorption on methylated silica

A: spectrum of almost totally methylated pure Cab-O-Sil silica, initially activated at 800°. B: after exposure to 20 Torr methanol at 30°.

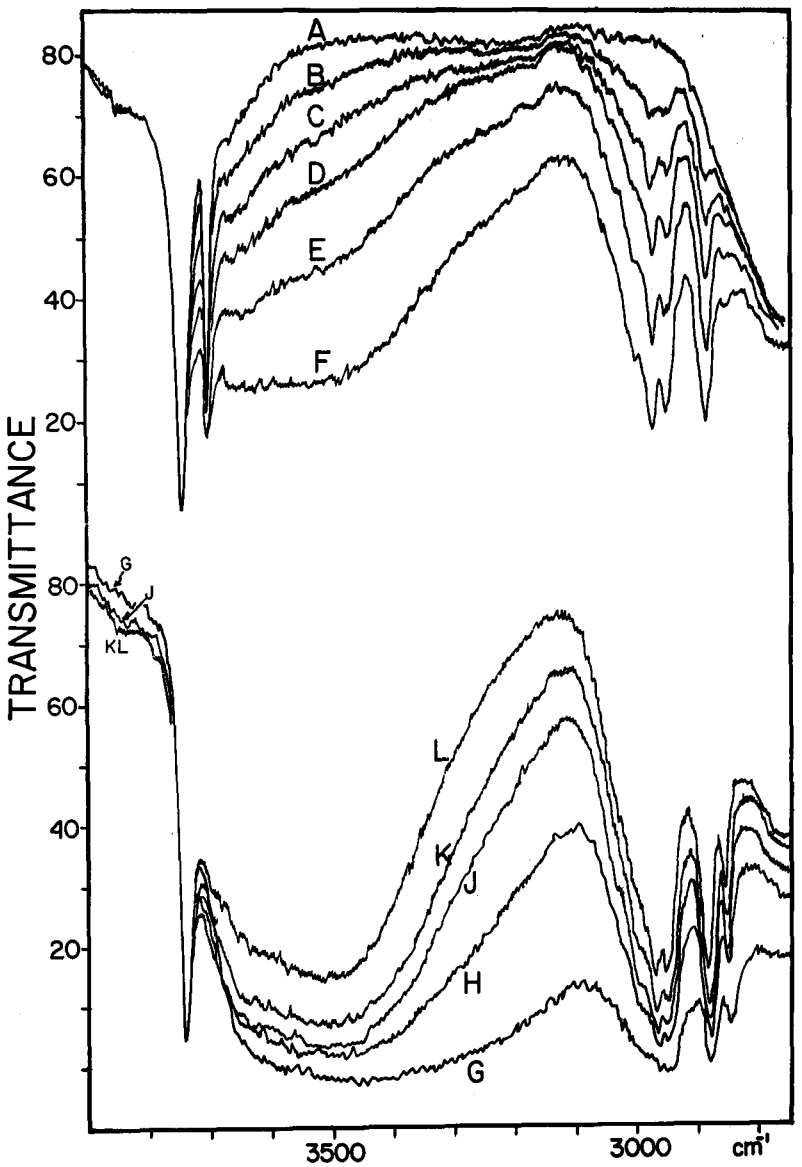


Fig. 5. Methanol sorption on porous glass

The spectra of Figs. 5 and 6 illustrate effects observed on sorbing methanol at 30° and then degassing under progressively more severe conditions. After the "background" spectrum A of the highly dehydroxylated sample had been measured, the sample was exposed vapor for 30 mins. at the following pressure in μ:

B: 27; C: 70; D: 130; E: 400; F: 1000; G: 6 Torr, after 14 hrs. The pressure was then reduced to 400 μ and spectrum H was recorded after 20 mins. Then, 20 mins. after the pressure was reduced to 30 μ, spectrum J was recorded. The cell was then opened to the pumps, and the sample was degassed at the following temperatures and times in hrs: K: 30°, 40; L: 100°, 20; M: 200°, 20; N: 300°, 20; P: 400°, 10; R: 500°, 10.

Porous Glass

A variety of experiments were carried out with highly dehydroxylated porous glass (usually degassed for at least 15 hrs at 750°). Some results dealing with low temperature adsorption and subsequent degassing are shown in Figs. 5 and 6. The effect of temperature on the surface methylation was also

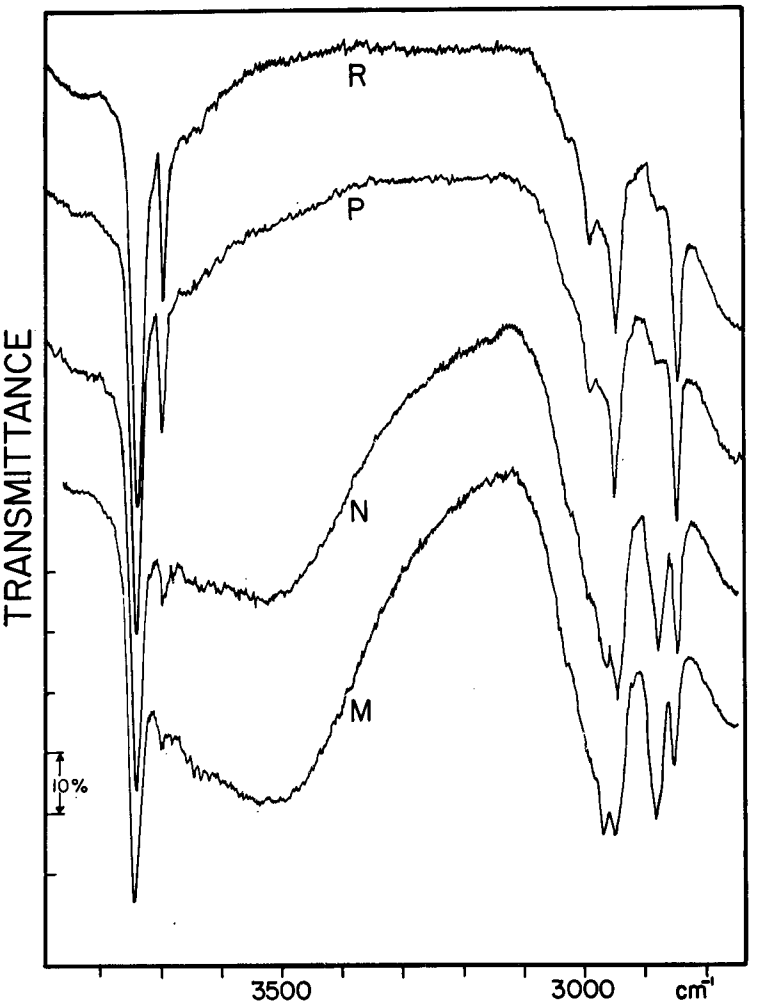


Fig. 6. Methanol desorption from porous glass

Continuation of the sequence of Fig. 5. The degassing temperature and time in hrs were: M: 200°, 20; N: 300°, 20; P: 400°, 10; R: 500°, 10. The ordinates were displaced to avoid overlapping of traces. The transmittance was 80 % at 3900 cm^{-1} for each spectrum.

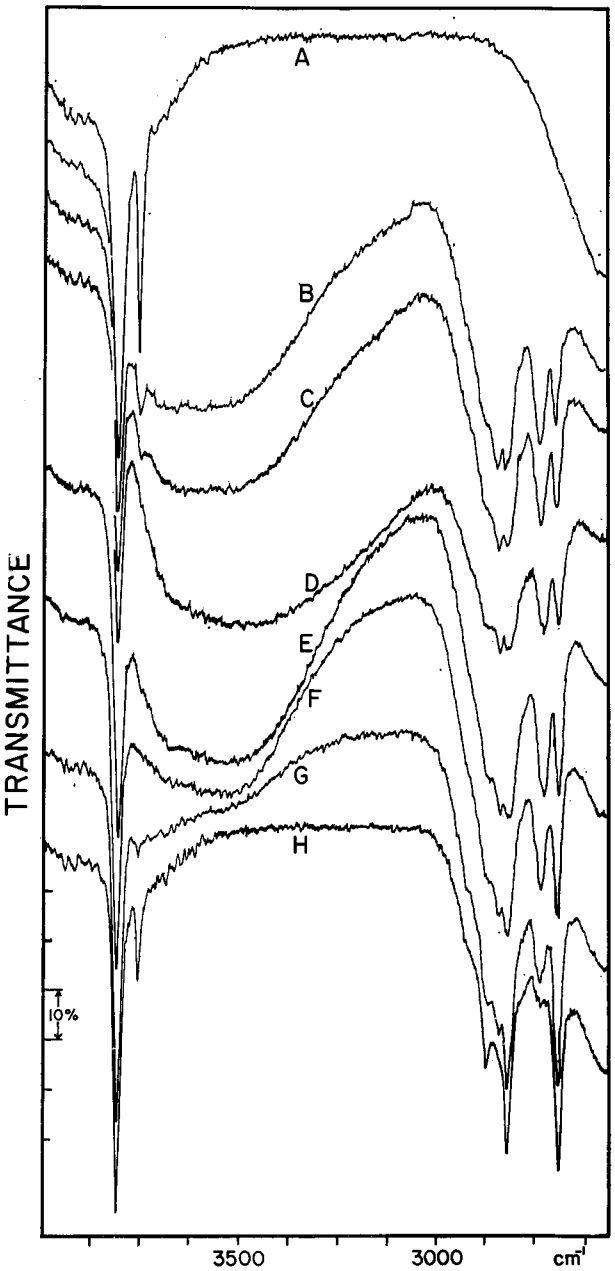


Fig. 7. Porous glass-methylation at 400°

After the background spectrum A had been recorded, the sample was heated at 400° in 1 Torr methanol for 1 hr. During that period, the gas phase was removed and replaced 8 times with fresh methanol in order to minimize the back reaction. After cooling to 30°, spectrum B was recorded. Spectra C and D were recorded after additional treatments of 1 hr each (6 exchanges of gas phase each). The sample was then degassed at the following temperature and times in hrs.: E: 30°, 15; F: 100°, 1 plus 200°, 1; G: 400°, 1; H: 600°, 1. The ordinates are displaced to avoid overlapping of traces. The transmittance at 3900 cm^{-1} is 82% for each spectrum.

examined. Some results on methylation at 400° shown in Fig. 7; these are typical of results obtained from 100° to 500°, and differ mainly in the rate and extent of methylation at various temperatures. The various results with porous glass can be summarized as follows.

(a) Methanol sorption at 30° did not cause any significant changes in the 3748 cm^{-1} SiOH band. During the sorption, *e.g.* spectra A to G, Fig. 5, the SiOH band broadened sightly, but this broadening seems to be mainly caused by the formation of a "tail" on the low wavenumber side of the SiOH band. The tail in the 3700–3500 cm^{-1} region, most apparent in spectra B and C of Fig. 5, is merged at higher methanol coverages with a broader band centering near 3500 cm^{-1}, *e.g.* specta C–F, Fig. 1. At the highest coverage the band spreads from 3700 to 3000 cm^{-1}, *e.g.* spectrum G, Fig. 5. Much of the methanol causing absorption in the 3500–3000 cm^{-1} range can be removed easily *e.g.* spectra G–L, Fig. 5, and is taken to be physically adsorbed methanol weakly bound by hydrogen bonds.

(b) A band forms near 3600 cm^{-1} at intermediate stages of sorption, *e.g.* spectra D, E, Fig. 5, but then becomes merged with the broader 3500 cm^{-1} band at higher coverages. The 3600 cm^{-1} band reappears on desorption, although indistinctly, *e.g.* spectrum N, Fig. 6.

(c) Desorption at 200° removes most of the adsorbate responsible for the 3500 cm^{-1} absorption. The latter is taken to be brought about by hydrogen-bonded methanol, much as is the case with silica.

(d) Methanol sorption caused pronounced changes in the 3703 cm^{-1} band attributed to surface B–OH groups.[8,9] As shown in the sequence of spectra A to G of Fig. 5 and A to D of Fig. 7, the B–OH band broadened, shifted to 3700 cm^{-1}, and disappeared on progressively increasing the amount of sorbed methanol. The B–OH band reappeared on desorption subsequent to sorption at 30°, as in spectra M to R of Fig. 6, but at decreased intensity. However, on degassing a specimen subsequent to a high temperature reaction, the B–OH band did not reappear until a temperature of 400° was reached *e.g.* spectrum G, Fig. 7. That temperature is much higher than the 200° degassing temperature required to remove physically adsorbed methanol from silica. The B–OH band grew on degassing at higher temperature, *e.g.* spectrum H, Fig. 7, but was then much diminished in intensity with respect to that found with the freshly degassed adsorbent. Also, in all cases of reaction of porous glass with methanol over the temperature range 30–400°, the B–OH band was diminished in the fashion shown by the spectrum of Figs. 5–7; the SiOH band was not significantly changed unless relatively long reaction times at 400° were employed.

(e) The spectra of methanol on porous glass differed significantly in the C–H region from those of methanol on silica in that 2 additional bands were observed. A prominent band appeared near 2884 cm^{-1}, shifted to 2879 cm^{-1} with increasing coverage and, on desorption, shifted to 2886 cm^{-1}. A second, less distinct band was observed near 2973 cm^{-1}, shifted to 2967 cm^{-1} with increasing coverage, and then shifted to 2973 cm^{-1} on degassing. The intensity changes of the 2973 cm^{-1} band are difficult to define because of strong overlapping with the 3000 and 3959 cm^{-1} bands.

Significant changes occurred in the C–H region on degassing at temperatures above about 200°. The 2973 and 2886 cm^{-1} bands declined with increasing temperature; simultaneously the 2959 and 2855 cm^{-1} bands attributed to surface Si–OCH_3 groups grew in intensity. Such effects are plainly visible in the spectra of Figs. 6 and 7.

Similar bands were found in spectra of methanol sorbed on boria-impregnated Cab–O–Sil. Some results obtained with a Cab–O–Sil sample containing 2 weight % boria are shown in Fig. 8. In general, the effects observed with methanol sorption on 2% $B_2O_3 \cdot SiO_2$ were entirely like those described for sorption on porous glass. The new bands in the C–H region could be ex-

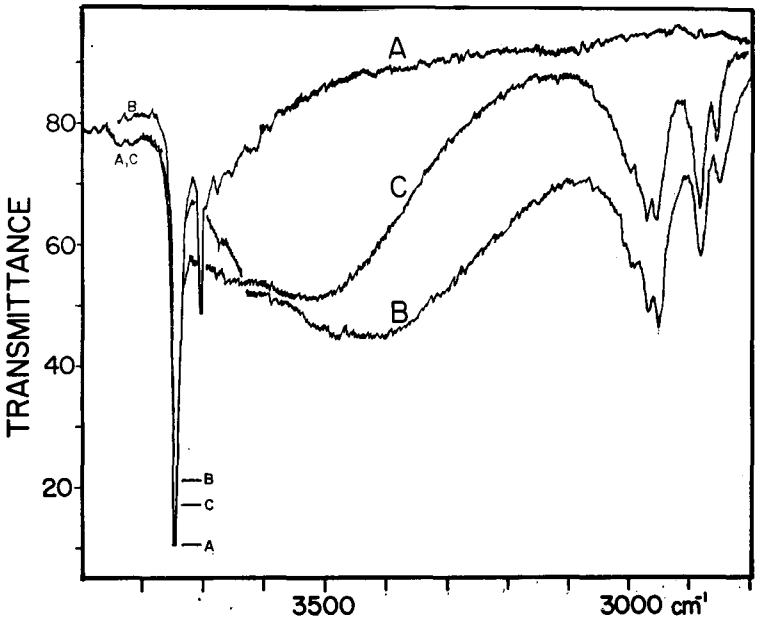


Fig. 8. Methanol sorption on 2% $B_2O_3 \cdot SiO_2$

A: after degassing at 750°, 15 hrs. B: after exposure to 20 Torr methanol at 30°. C: after degassing at 30° for 1 hr.

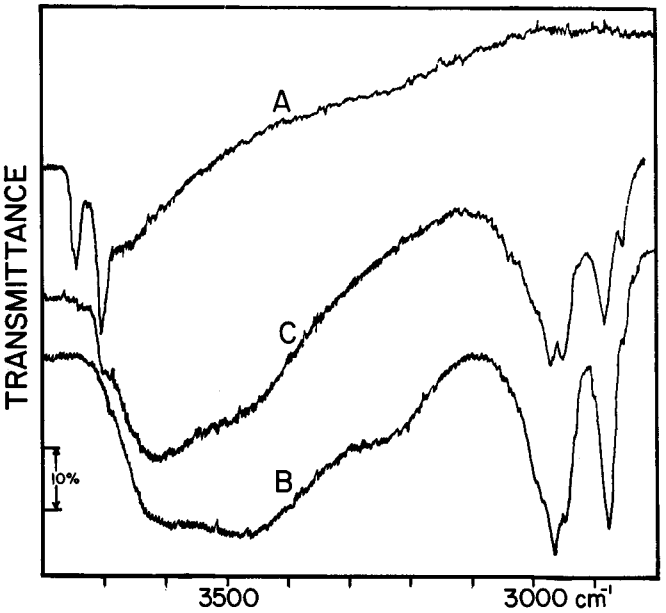


Fig. 9. Methanol sorption on 20% $B_2O_3 \cdot SiO_2$
A: after degassing at 400°, 1 hr. B: after exposure to 20 Torr methanol at 30°. C: after degassing for 20 hrs at 30°.

aggerated by sorbing methanol on Cab-O-Sil containing 20 weight % boria. Some results are shown in Fig. 9. Spectrum A of Fig. 9 shows both SiOH and B-OH bands, but the SiOH band is much smaller than that found with the 2% $B_2O_3 \cdot SiO_3$ sample. The large amount of boria probably covered most of the surface silanols. Adsorption of methanol on such a surface then brought about the large 2973 and 2886 cm^{-1} bands shown in spectrum B of Fig. 9.

Reactions on Porous Glass

The reactions occurring on porous glass are some what more complicated than those found with silica, and are attributed to the presence of boria on the porous glass surface. Porous glass is known to contain some boria[23] which can migrate to the surface and effect the surface properties of the glass.[8~15] As the new bands found with porous glass can be induced with silica by impregnating the silica with boria, the differences found between the behavior of pure silica and porous glass are attributed to the presence of boria on the glass surface. Consequently, the new bands are assigned to C-H stretching frequencies of methanol adsorbed on boria present on the porous glass, in analogy to the suface structures formed on pure silica. The assingnments are

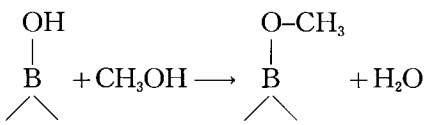
TABLE I. CH_3 Stretching Frequencies for Methanol Adsorbed on Porous Glass

State	Symmetric Mode (cm^{-1})	Asymmetric Mode (cm^{-1})
Chemisorption, B–O–CH_3	2886	2973
H-bonded to B–OH	2379	2967
Chemisorption, Si–O–CH_3	2855	2959
H-bonded to SiOH	2845	2950

summarized in Table I.

As far as physical adsorption is concerned, it seems reasonable to assume that hydrogen-bonded structures similar to those described for adsorption on silica would be formed on porous glass by bonding of methanol to B–OH groups. Our spectra of porous glass do not show bands specifically attributable to perturbed B–OH groups and distinguishable from perturbed SiOH groups. This is not unexpected, in view of the heterogeneity of silica[17] and the even greater heterogeneity of porous glass. Physical adsorption effects on the boria and silica portions of the porous glass are thus spectroscopically indistinguishable and might be taken to be additive. However, the various results indicate that the presence of boron does not merely premit the formation of adsorbed species similar to those formed on silica.

Spectra of methanol sorption at low temperature on porous glass clearly show that B–OH groups were greatly perturbed, while SiOH groups remained largely unaffected. Similarly, reaction with methanol at higher temperatures again predominantly affected B–OH groups, SiOH groups remaining largely unaffected until the reaction conditions became quite severe. Note that the B–OH band was diminished after a low-temperature sorption-desorption cycle (Figs. 5, 6), and also did not reappear until a relatively high degassing temperature was reached subsequent to a "reaction" (Fig. 7). Such preferential attack on the B–OH groups, along with the relatively small bands due to Si–OCH_3 implies that the esterification reaction



V

occurred to a greater extent than reactions I or IV. Presumably, a reaction analogous to reaction IV could also occurr relatively easily. The B–OH groups would appear to be more labile than SiOH groups, so that reaction V could

occur to a significant extent at room temperature. Some support for this comes from the observation of the band near 3600 cm^{-1}. Water sorption on porous glass brought about a distinct band near 3600 cm^{-1} which was attributed to H_2O adsorbed on boron on the glass surface[12]. The 3600 cm^{-1} band found with methanol adsorption could have been produced by H_2O formed *via* reaction V. The "tail" at the low frequency side of the SiOH band observed at low coverage could be due to hydrogen-bonded hydroxyls formed by the dissociation of chemisorbed water formed via reaction V.

The changes occurring in the C–H region on degassing are of special interest. As noted earlier, above 200° or so, when all or most of the hydrogen-bonded methanol had been desorbed, the bands attributed to B–OCH_3 species decreased while those attributed to Si–OCH_3 species *increased*. It is likely that some conversion of physically adsorbed methanol to Si–OCH_3 groups occurred during the early stages of degassing at medium temperature; this would cause an increase in the Si–OCH_3 bands. However, the 2973 and 2886 cm^{-1} bands attributed to B–OCH_3 could be observed after degassing at 400°, *e.g.* spectrum G, Fig. 7. In view of the relative ease of desorbing hydrogen-bonded methanol, it is improbable that physically adsorbed methanol was solely responsible for the growth of the Si–OCH_3 bands. This effect is attributed to the destruction of B–OCH_3 groups above 200°. It is suggested that B–OCH_3 groups decomposed to form methyl radicals, which then reacted at suitable sites to form Si–OCH_3 groups. As some evidence has been presented to indicate that the boron is present in boria aggregates on "islands" on the porous glass surface[12,14], the reaction to form Si–OCH_3 groups would involve some diffusion of radicals from the islands to the silica portion of the surface. Islands of methylated boria would thus act as sources of reactant.

Another effect is apparent. Various spectra show that physically adsorbed methanol desorbed at 200°, at surface Si–OCH_3 groups could only be eliminated slowly at temperatures of 600–700°. However, when a sample from which physically adsorbed methanol had been removed was heated at 600°, some B–OH groups were formed, *e.g.* spectrum H, Fig. 7. As the surface Si–OCH_3 groups are the only obvious source of hydrogen, the effect points to a degradation of Si–OCH_3 on the porous glass surface. This would imply a transfer of hydrogen atoms to suitable sites on boria islands at which B–OH groups could form. A similar degradation has been observed with methylated silica, and is at present under investigation.

Acknowledgement

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