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Investigations of Molecules Trapped in Microporous Alumina Aerogels

I. Infrared Spectroscopic Studies

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Alumina aerogels were made by the conventional method which involves removing organic molecules in an autoclave above their critical temperature. The infrared spectra of the resulting products show that some of these molecules are trapped in the alumina presumably in molecular-sized micropores. On heating, the trapped molecules decompose to give carbonaceous residues and unsaturated hydrocarbons which can be oxidized by adding air or oxygen. For alumina aerogels prepared using alcohol, the product of oxidation is carbon dioxide which remains trapped in the micropores giving rise to a characteristic adsorption band at 2346 cm^{-1}: all other aerogels fail to retain carbon dioxide in this way.

Some conclusions about the state of trapped molecules are derived from the study of their spectra compared with those of the solid and liquid states.

INTRODUCTION

Following the publication by Peri and Hannan (*1*) in 1960 of a method of preparation of alumina aerogels for spectroscopic work, such aerogels have been used in the present author's laboratory in recent years for infrared spectroscopic studies of gases adsorbed on alumina. It was observed that these aerogels normally had an apparent infrared absorption band at ca. 2340 cm^{-1} which could not be removed by heating up to 500°C. Subsequent use of a high resolution grating spectrometer (*2*) showed that the band was quite sharp and moderately strong (absorbance 0.1–0.3). The position of the maximum absorption was 2346 cm^{-1} and there was no indication of rotational fine structure. Thus, atmospheric carbon dioxide was not responsible for the absorption nor was it caused by lack of balance between the two beams of the spectrometer. Furthermore, aerogels made by a slight modification of the usual method showed no such absorption.

Examination of the differences between the two types of aerogel, indicated by their nitrogen adsorption isotherms, showed that their pore structure was entirely different, one having a much more open structure than the other. The absorption at 2346 cm^{-1} was thus provisionally assigned to carbon dioxide molecules trapped in sealed-off micropores, following the original suggestion of Peri and Hannan (*1*). More recently, Low, Maddison and Ramamurthy (*3*) have reported the trapping of carbon dioxide in gels of germanium dioxide. Furthermore, Wood and Nassau (*4*) have shown that not only carbon dioxide but also water is trapped in molecular-sized holes in single crystals of beryl and both give sharp infrared absorption bands characteristic of single molecules interacting with the alumino-silicate environment. Cannings (*5*) has also found that it is very difficult to remove water from sepiolite even after evacuation at 400°C, as shown by the 1616 cm^{-1} band, characteristic of the bending mode of water, persisting at this temperature. Finally, Pliskin, Simmons and Esch (*6*) have observed that carbon dioxide can be trapped in RF-sputtered silica films, where it gives a very sharp infrared absorption band at 2340 cm^{-1}. In all cases this type of trapping is similar to that occurring in the so-called clathrate compounds.

In this paper, we have pursued the investigation into the structure of the alumina aerogels further, investigated the origin of the carbon dioxide absorption band and shown that other molecules may be trapped in a similar way.

EXPERIMENTAL METHODS

Infrared Spectra

A Grubb Parsons DB3/GS2 grating spectrometer was used, calibration of which was carried out with the absorption peaks of atmospheric water vapor and carbon dioxide: the total measurement error was within the limits of ±2 cm^{-1}. Some of the broader bands, however, are quoted to ±5 cm^{-1}. The monochromator was flushed with dry nitrogen to increase the sensitivity in the regions of atmospheric absorption, particularly by carbon dioxide.

A simple absorption cell, described in detail elsewhere (7), was used. Heating was carried out in the upper part of the cell by a small furnace wound directly around silica tubing. Temperatures of up to 900°C were easily obtained in this way. The aerogel was placed in a silica holder which could be moved up and down magnetically by a sealed-in soft iron core. All spectra were taken at room temperature.

Sample Preparation

Alumina aerogels were generally prepared after the method of Peri and Hannan (*1*) and Peri (*8*). A stock alumina sol, made by dissolving 99.9% pure aluminium in analytically pure acetic acid activated by mercury, was converted into an aquagel by exposure to ammonia vapor. The sol was floated on top of carbon tetrachloride in a petri dish which was placed in a desiccator containing well-diluted (about 1:10) aqueous ammonia solution. Provided that the concentration of the ammonia vapor was approximately correct, the gelation took place overnight to give a clear, firm aquagel. We confirmed Peri's observations (*8*) that too long an exposure to ammonia vapor or to too high a concentration produced a white, opaque gel which tended to crack.

The aquagel was then immersed for 3 days in doubly distilled ethanol, which was changed every day. The corresponding aerogel was produced by heating the alcogel in an autoclave in the presence of excess ethanol to 250°C. This is just above the critical temperature of alcohol (*9*) (243°C) and by releasing the pressure at this stage, the alcohol can be removed without the gel structure collapsing (*10*). The end product is the so-called aerogel, a very light, microporous gel with the physical shape of the original aquagel. In some cases, the alcohol was further displaced by diethyl ether (critical temperature, 194°C) which was removed from the gel in a similar manner. Again, the ether was displaced in other samples by *n*-hexane (critical temperature, 234°C) or by isopentane (187°C).

Sample Treatment

Because previous aerogel samples showed bands at 2346 cm^{-1} only after being heated in air at 600°C, it was decided to investigate at what stage carbon dioxide was formed and whether it arose from the decomposition and oxidation of occluded ethanol (or ether) used in the preparation. Accordingly, samples taken straight from the autoclave without pretreatment were heated from 200 to 900°C in steps of 100°C. Heating was carried out for 2 hr periods. The time was chosen as being experimentally convenient; it had no other significance. Samples were heated first of all *in vacuo* (ultimate pressures ca. 10^{-6} Torr). An identical sample was then heated in about 140 Torr of pure, dry oxygen, approximately the partial pressure of oxygen in the air. In this case, after the heating period of 2 hr, the sample was evacuated hot for 5 min before cooling to take the spectrum, in order to remove any products of the heat treatment.

Sample Analysis

X-Ray diffraction analysis of the phase of the samples was carried out by the Analytical Research Group of these laboratories. Confirmation of the analysis was obtained by firing the samples at high temperatures (900–1400°C), and redetermining the phase of the high temperature product (Table 1). In addition to these samples, many others have been used, most of them made via ethanol, which were found to be principally in the γ phase after calcination at 600°C. The samples were also investigated by electron microscopy and by analysis of the gravimetric adsorption isotherms with nitrogen and carbon tetrachloride as adsorbates. These results will be discussed fully in Part II.

Deuteration of Alumina

In order to see the details of the absorption spectra of trapped ethanol more clearly, a sample of aerogel from Batch II (see above) was treated with deuterium for a total of 76 hr in a pressure of 132 Torr at 250°C. Five changes of deuterium were used, the sample being evacuated for a few minutes before fresh gas was added.

RESULTS

X-Ray Analysis

Aerogels made in the manner described in this paper yield alumina largely in the γ phase. This is somewhat surprising, as the aerogels were analyzed straight after removal from the autoclave, with no further treatment. As the maximum temperature attained in the autoclave was only 250°C, one might expect to see boehmite rather than γ-alumina. It is possible that in the high pressures of alcohol and ether reached in the autoclave (63 bar at 243°C for ethanol, 35 bar at 194°C for ether) a hydrothermally accelerated phase change may be occurring. The lower critical temperature required for isopentane (187°C), however, does result in boehmite as the end product. The alumina formed in sample II is not usually the predominant phase formed in this kind of preparation so to some extent the sample is anomalous. We do not, however, believe that the difference in phases between samples is significant as far as differences in ability to trap carbon dioxide molecules are concerned.

Infrared Spectra

Infrared spectra of samples from batch II (alcohol-prepared) and batch III (ether-prepared) are shown in Figs. 1 and 2: some curves for intermediate temperatures are omitted for the sake of clarity. Both these samples were heated in oxygen: samples heated *in vacuo* show similar bands but some of them persist longer. For example, in Fig. 1, the C–H bands at around 2900 cm^{-1} have almost disappeared when heated

TABLE 1
DETAILS OF STRUCTURE OF SAMPLES USED

No. of batch	Made via	Appearance	Phase
I	Ethanol	White, opaque	$\gamma + \text{little } \chi$
II	Ethanol	Clear, transparent	χ only. About 100–200 Å crystallite size
III	Ether	Clear, transparent	Poorly crystalline γ
IV	Ether	White, opaque	$\gamma + \chi$(trace)
VIII	*n*-Hexane	Clear, transparent slightly yellow	Not determined
IX	Isopentane	Clear, transparent, white	Boehmite crystallite size about 50 Å

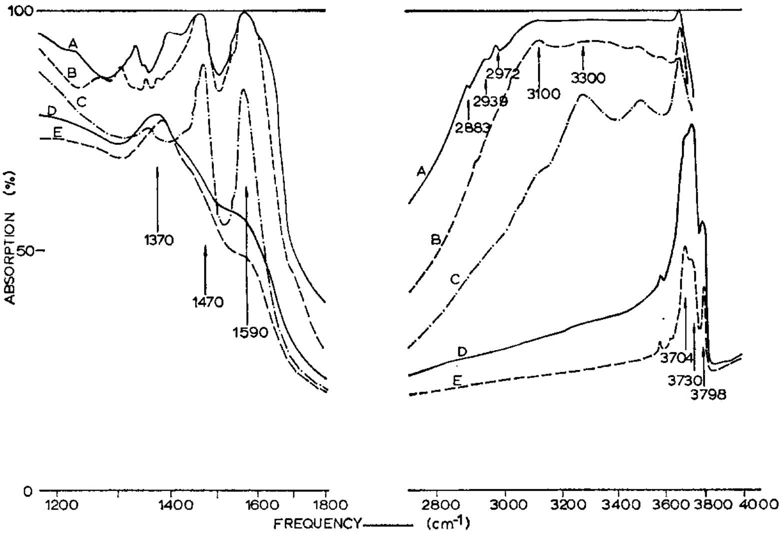


FIG. 1. Infrared absorption spectrum of alcohol-prepared alumina aerogel (batch II) after heating in oxygen for 2 hr to temperatures shown. (A) After removal from autoclave; (B) 300°C; (C) 400°C; (D) 600°C; (E) 800°C.

to 300°C in oxygen (curve B) whereas in a similar sample heated *in vacuo* they persist up to 500°C.

In the same way, the very intense "alumina" bands at about 1590 and 1470 cm^{-1} (Figs. 1 and 2, curves A, B, C) are completely removed by heating in oxygen at 500°C, whereas *in vacuo* 600°C is required to produce the same effect (*11*). When these bands are removed, a residual very broad and weak band remains at about 1590 cm^{-1} [Fig. 1 (D)]. The spectra between 2000–1100 cm^{-1} become less complex in all cases as the temperature is raised. Once the temperature has reached 700°C, apart from the band at 1590 cm^{-1} only a

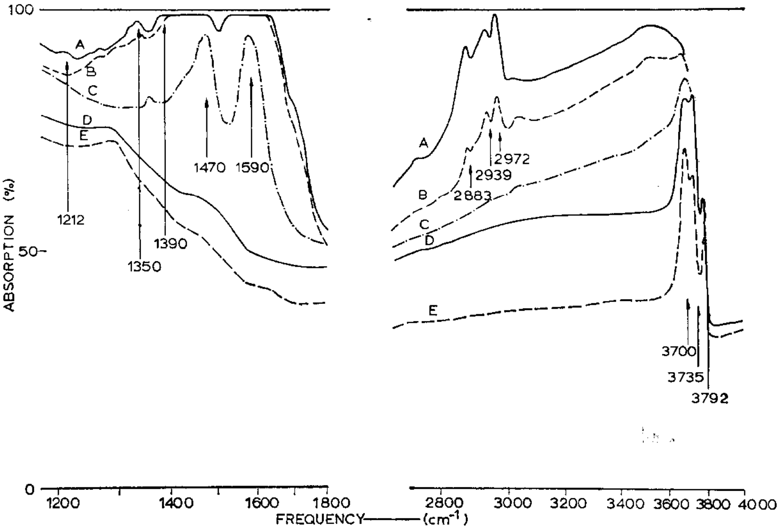


FIG. 2. Infrared absorption spectrum of ether-prepared alumina aerogel (batch III) after heating in oxygen for 2 hr to temperatures shown. (A) 200°C; (B) 300°C; (C) 400°C; (D) 600°C; (E) 700°C.

broad band of medium intensity remains (at 1370 cm^{-1}).

No correlation between the C–H stretching bands and absorption bands below 2000 cm^{-1} was found for alcohol-prepared aerogels (batches I and II). For ether-prepared aerogels, on the other hand, some of the bands found below 1400 cm^{-1} (1390, 1350, 1212, 1163 cm^{-1}) may be caused by CH_3 deformation and C–O stretching bands (*12*).

The O–H stretching region showed very complex changes for both kinds of aerogel. Some of the initial very broad absorption at about 3600 cm^{-1} may have been due to molecular water retained in micropores even at 200°C. This was particularly true of the alcohol-prepared aerogel where there was a pronounced shoulder at 1640 cm^{-1} (the HOH deformation frequency) [Fig. 1 (A)].

Of the remaining broad absorption above 3400 cm^{-1}, Figs. 1 and 2 show how the surface –OH groups are progressively removed as the temperature is increased. At higher temperatures (700–800°C) three distinct peaks remain, at 3792, 3735, and 3700 cm^{-1} for γ-alumina and 3798, 3730, 3704 cm^{-1} for χ-alumina. It is possible that the differences in frequency are not significant. These values agree very well with those of Peri and Hannan (*1*) (3795, 3737, 3698 cm^{-1}) and of Peri (*8*) (3800, 3780, 3744/3733, 3700 cm^{-1}).

Other broader bands between 3300 and 3100 cm^{-1} in the alcohol-prepared aerogel (Fig. 1) gradually decrease in intensity concurrently with the C–H bands.

The C–H region at 3000 cm^{-1} shows some consistent features. The main C–H frequencies are practically identical for both the alcohol- and ether-containing aerogels at 2972, 2939, 2883 cm^{-1} (all ±2 cm^{-1}). In a deuterated alcohol-prepared aerogel (sample II, Fig. 3), where the obscuring background of the broad OH bands was removed, a smaller band was revealed at 2863 cm^{-1}. The C–H bands were all much stronger for ether than for alcohol. The corresponding $-CH_2-$ and $-CH_3$ deformation modes were not positively identified because of the strong background absorption near 1400 cm^{-1}.

Very weak bands at 2747 ± 7 cm^{-1} and 2545 cm^{-1} did disappear with the main C–H stretching bands of ether [Fig. 2 (A–

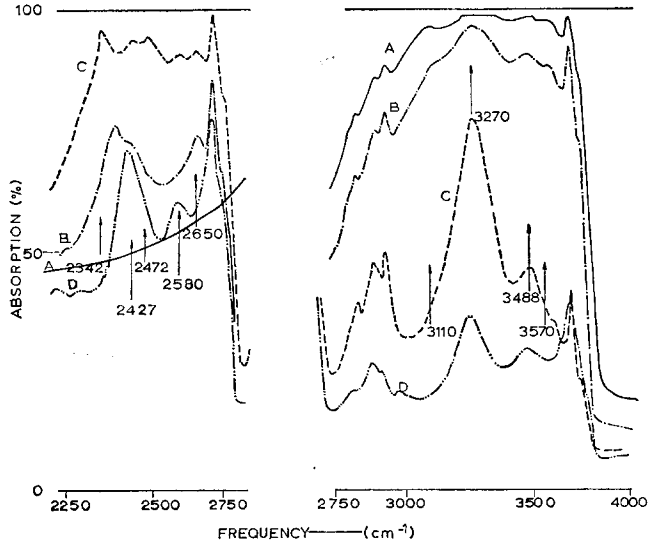


FIG. 3. Infrared absorption spectrum of deuterated alcohol-prepared alumina aerogel (batch II). (A) Before deuteration; (B) after exchange in 132 Torr D_2 at 250°C for 20 hr; (C) after exchange in 132 Torr D_2 at 250°C for 76 hr; (D) after heating (C) in vacuum for 2 hr at 400°C.

C)]. They were not present in the alcohol-containing aerogel and no band assignment can satisfactorily be given to them.

Weak, broad bands in the region 3040–3060 cm^{-1} were observed for both kinds of aerogel on heating above 200°C although they were more marked for ether-containing samples (Fig. 2) and also on heating *in vacuo* rather than in oxygen. Bands in this region are characteristic of C–H stretching frequencies of unsaturated hydrocarbons (*12*).

Isopentane- and *n*-hexane-prepared aerogels gave similar results to the ether-prepared ones. C–H bands were found at the lower temperatures and after heating the samples turned black. Neither sample gave a band corresponding to trapped carbon dioxide on heating in oxygen at 600°C.

Deuterium Exchange Experiments

As there seemed to be a large number of –OH groups in the alcohol-containing aerogel, an attempt was made to remove the –OH groups belonging to the alumina surface by selective deuteration with D_2 as this proceeds quite smoothly between 200–300°C (*1, 8, 11, 13*). Curve C (Fig. 3) shows the result of deuteration at 250°C for a total of 76 hr in 132 Torr deuterium. Exchange at 200°C was too slow to be practicable and as partial exchange of the –OH groups tentatively assigned to the alcohol was occurring even at 250°C we did not raise the exchange temperature to 300°C or proceed to complete exchange of the alumina –OH groups. Curves A and B show the results of intermediate deuteration runs, and curve D the spectrum after the deuterated sample had been heated *in vacuo* to 400°C for 2 hr.

The following bands (with the corresponding –OH band in parentheses) found after deuteration were 2650 (3570), 2580 (3488), 2427 (3270), 2472 (—), 2342 (3110). The isotopic shift ratio was about 0.74 in each case. There was no C–H band replacement by C–D.

On heating at 400°C (curve D), the 2650, 2472 and 2342 cm^{-1} bands were completely removed, leaving only the 2580 and 2427 cm^{-1} bands together with their corresponding –OH bands (3488 and 3270 cm^{-1}). Formation of the weak band at around 3040 cm^{-1} indicated, as before, the presence of unsaturated hydrocarbons.

The hydroxyl and deuteroxyl bands of the alumina surface call for no special comment. Because of the low temperature of the heat treatment imposed by the deuteration, the –OH and –OD bands are not found at the positions described previously. The lowest frequency band (3672 cm^{-1}) proved the most resistant to deuteration.

Formation of Carbon Dioxide Bands

As previously mentioned, aerogels made only by the ethanol preparation route give a strong band at 2346 cm^{-1} after heating in oxygen or air at 600°C. Aerogels in which the alcohol had previously been replaced by diethyl ether, isopentane or *n*-hexane did not give this band. It appeared only after heating at 600°C: there was no sign of it after heating at 500°C.

The shape of a typical band is shown in Fig. 4. The spectrometer spectral slit width was 2.5 cm^{-1} and the measured bandwidth of the peak $(\Delta\nu_{1/2})$ was 20 cm^{-1}. The scanning rate of the spectrometer was 18 cm^{-1} min^{-1}. Reducing the spectral slit width

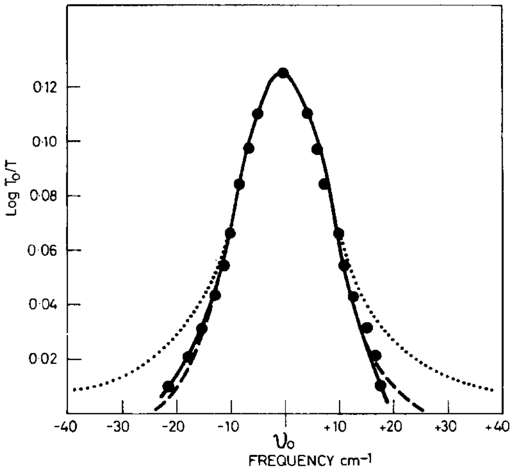


FIG. 4. Infrared absorption band of trapped carbon dioxide in alumina aerogel. (——) Experimental curve; (····) best fitting Lorentzian curve; (- - -) best fitting Gaussian curve.

to 1.25 cm^{-1} made no difference to the shape of the band.

Also included in Fig. 4 are Gaussian and Lorentzian contours (*14*), fitted to the peak absorbance and the half bandwidth in the latter case and peak absorbance and bandwidth at $1/e$ of peak absorbance in the former. As shown, the former gives a good approximation to the observed band, whereas the latter is completely inaccurate once the band diverges appreciably from ν_0 (2346 cm^{-1}).

Heating the aerogels to 1000°C reduced the intensity of the band by about 25%.

Discussion

Spectra of Trapped Molecules

The experiments described above have shown that alumina aerogels entrap liquid organic compounds used in their preparation. The molecules of these compounds decompose on heating and react with oxygen to form carbon dioxide which in most cases diffuses out through the pores of the gel. In aerogels made via the ethanol route, it would seem that the pores are insufficiently wide to let the gas out and a band appears at 2346 cm^{-1}, close to the ν_3 gas-phase band (*15*) at 2349 cm^{-1} and the solid phase band (*16*) at 2342 cm^{-1}. As shown by comparison with the gas and solid phase spectra, the band is narrow ($\Delta\nu_{1/2} = 20$ cm^{-1}), although not so narrow as the latter ($\Delta\nu_{1/2} = 6$ cm^{-1}) but shows no sign of the gas-phase rotational P and R branches.

Some additional information on shapes of the ν_3 CO_2 band has been provided by Cunliffe-Jones (*17*). He found that the bandwidth of dissolved CO_2 increased from 6 cm^{-1} in polar organic solvents to 20 cm^{-1} in nonpolar ones because of contributions from rotation. This value is comparable to the values found here for trapped carbon dioxide but whereas the shapes of the bands in this work are Gaussian, those in solution are Lorentzian. Cunliffe-Jones postulated that a slight asymmetry in the band shape (found also in our results), was due to contributions on the low frequency side from "hot bands." Pliskin, Simmons and Esch (*6*) found that the bandwidth of carbon dioxide dissolved in water was small, only 9.3 ± 0.2 cm^{-1}. When the gas was embedded in evaporated silica, the bandwidth was even narrower, 7.4 cm^{-1}. The absorption band of CO_2 trapped in beryl also has a very narrow bandwidth [about 10 cm^{-1}, taken from Fig. 8 of ref. (*4*)] but has considerable rotational "wings." The spectrum of carbon dioxide in the cages of the CO_2–quinol clathrate has a well-marked rotational structure (*18*).

In all these cases, it is clear that we are seeing single carbon dioxide molecules in a matrix where restricted rotation is allowed. The band due to carbon dioxide trapped in aerogels is much broader and has a different shape. Unfortunately, no data on the spectrum of liquid carbon dioxide are available but as the band does not quite resemble either the solid phase band or that of restricted rotation in a matrix, we suggest that, by extrapolation, it might be similar to that due to *quasi*-liquid carbon dioxide.

A small band at 3588 cm^{-1} which appears at the same time as the band at 2346 cm^{-1} [Fig. 1(D)] was tentatively assigned to the ($\nu_3 + 2\nu_2$) combination band, which appears at 3609 cm^{-1} in the gas phase (*15*). Examination of previous aerogel spectra, however, failed to confirm the existence of this weak band and this assignment must be regarded as rather dubious. The assignment of the 2346 cm^{-1} band to the ν_3 stretching mode of carbon dioxide is positively confirmed, however, by the detection of a very weak band at 2284 cm^{-1} This is identical to that found by Yamada and Person (*16*) for solid carbon dioxide at the same frequency and intensity ratio, and identified by them as the ν_3 mode of $^{13}CO_2$.

As we were dealing with the possibility of molecular-sized micropores in alumina aerogel being responsible for trapping molecules, the possibility of some sort of molecular sieve effect had to be considered. Ward and Habgood (*19*) have investigated the spectra of carbon dioxide on molecular sieves and found two or three bands in the region of the gas-phase band. The strongest band was assigned to single carbon dioxide molecules polarized in the field of the metal ions of the sieves used. The maximum loading of the sieve was 4.4 molecules of carbon dioxide/cavity but even at a loading of only 1.1 molecules/cavity the three bands were well developed on a BaX type sieve. The assignment of the strong band to polarized carbon dioxide molecules was confirmed by Angell (*20*) by analogy with the results of Angell and Schaffer (*21*) on carbon monoxide adsorbed on molecular sieves. In both cases a linear relation was obtained between the frequency of the most intense band of the adsorbed molecule and the computed electrostatic field within the cavities of the sieves. The smaller side bands below the main frequency were explained by Angell and Schaffer in terms of adsorption of CO dipoles onto surface oxide ions having, respectively, the carbon and oxygen atoms attached. Ward and Habgood could find no convincing explanation for their side bands in the case of carbon dioxide but presumably the same reasoning as above could well apply.

Comparison with the present results shows no resemblance either in the shape of the relevant bands or the appearance of side bands other than the small band at 2284 cm^{-1} which falls exactly on the expected isotope band for ν_3 $^{13}CO_2$. Furthermore, Ward and Habgood mention the fact that at higher pressures of adsorption a new band appears at just below 2350 cm^{-1} which, with its ease of removal and proximity to the gas-phase band, corresponds to physical adsorption. There is, therefore, no reason to think that the spectrum of trapped carbon dioxide in alumina is due to the interaction of single carbon dioxide molecules with the electrostatic field within the micropores.

This conclusion is borne out by the spectra obtained by adding carbon dioxide to alumina aerogels heated to 800°C or above. At pressures up to about 2 Torr the main frequency of absorption of physically adsorbed carbon dioxide is at 2370 cm^{-1} as first observed by Peri (*22*). Our work has confirmed this and the spectra show that this additional band appears quite independently of the band at 2346 cm^{-1} which is obtained unchanged when the sample is evacuated [see Fig. 11 of Ref. (*22*)]. If, however, alumina is heated to less than 800°C the physical adsorption band is at around 2350 cm^{-1} and no spectroscopic distinction between the two types of absorption is possible. In other words, although the band due to the trapped molecules is similar to that due to physically adsorbed ones in general shape and position, the two are quite distinct and one is not affected by the other.

Trapped Organic Compounds

The detection of C–H bands in the spectra of uncalcined aerogels confirms the idea that the trapped CO_2 derives from oxidation of carbonaceous residues obtained by pyrolysis of the organic compounds used in the preparation of the aerogels. Although positive confirmation that the organic compounds are trapped in the form of free molecules is not possible because the "fingerprint" region of the spectrum is obscured by high background absorption, there is no reason to think that they are not so trapped particularly when the analogy of *quasi*-liquid CO_2 is taken into account. Moreover, alcohol trapped in aerogels shows an O–H stretching band (confirmed by deuterium exchange of the alumina –OH groups) at 3270 cm^{-1}, almost identical in position, intensity and shape with that of liquid (hydrogen-bonded) ethanol (*23*).

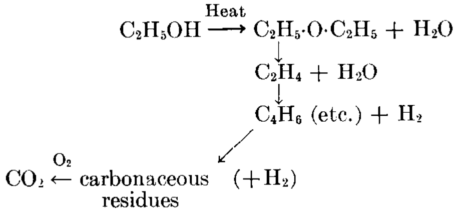
Although the position of the C–H bands for both trapped ethanol and ether is almost identical, this is not surprising since the absorbing group is C_2H_5O– in each case. Assignment of the bands as 2972 (CH_3 asymmetric stretch), 2939 (–CH_2 asymmetric stretch), 2883 (CH_3 symmetric stretch), 2863 cm^{-1} (–CH_2 symmetric stretch) follows (*12, 24*).

Comparison of the spectra of the trapped molecules with those of the gas and liquid phases shows that the liquid phase corresponds closely with that of the trapped molecules. This is particularly true of ethanol where the sharp, monomeric peak at 3600 cm^{-1} in the gas phase is changed by hydrogen bonding to 3300 cm^{-1} in the liquid phase, (cf. 3260–3270 cm^{-1} for the trapped molecules).

Decomposition of Hydrocarbons

Organic molecules trapped in this way show, on heating, a less and less intense absorption spectrum until at 500°C *in vacuo* all C–H bands have disappeared. At the same time the sample becomes very black. Concurrently with the disappearance of bands between 2700–3000 cm^{-1}, a new one appears at 3040–3060 cm^{-1}. This is a broad, rather indeterminate band at a position characteristic of unsaturated hydrocarbons. The irregular shape of the band means that probably more than one compound is involved in this absorption.

We can account for these phenomena by the following reaction scheme.



$$\begin{tikzcd}
 & C_2H_5OH \arrow[r, "\text{Heat}"] & C_2H_5\cdot O\cdot C_2H_5 + H_2O \arrow[d] \\
 & & C_2H_4 + H_2O \arrow[d] \\
 & & C_4H_6\ (\text{etc.}) + H_2 \arrow[dl] \\
CO_2 & \text{carbonaceous residues} \arrow[l, "O_2"'] & (+H_2)
\end{tikzcd}$$

In the presence of oxygen, the carbonaceous residue reacts to form carbon dioxide. Normally this can diffuse out from the pores but in alcohol aerogels alone it is trapped. We shall discuss this interesting difference in behavior between the alcohol and the other aerogels in a following paper.

The CO_2 band is formed either by heating the sample directly in oxygen to 600°C or by heating it *in vacuo* to, say 700°C and then heating it in oxygen at 600°C. The micropores are therefore accessible to molecular oxygen, at least, at 600°C and above. Hydrogen and water can diffuse out and are pumped away. We can say this with some certainty because we have never obtained spectra of trapped water at 1640 cm^{-1} on heating above 300°C.

Deuterated Alcohol Aerogels

The deuterium exchange experiments on uncalcined alcohol-prepared aerogels revealed that the hydroxyl stretching region was rather more complex than for ether- or hydrocarbon-prepared ones. It was possible to separate the hydroxyl and deuteroxyl frequencies, other than those associated with free (nonhydrogen-bonded) alumina frequencies, into two groups: those at 2650, 2472 and 2342 cm^{-1} (–OD groups), which appeared fairly rapidly and completely on heating in deuterium, and the two bands at 2580, 2427 cm^{-1} [original positions (3488 and 3270 cm^{-1})] which did so only slowly and partially. Furthermore, heating to 400°C *in vacuo* removed the first group completely whereas the second group was reduced only by about 60% of the original intensities.

The position of the 3270 cm^{-1} band and its great breadth and intensity mark it out as being the –OH stretching frequency of ethanol polymers resulting from strong intermolecular hydrogen bonding. Recent work by Barnes and Hallam (*25*) on matrix-isolated ethanol and deuteroethanol has shown that apart from the monomer band at 3660 cm^{-1}, the hydroxyl stretching region shows absorption bands at 3530 cm^{-1}—a fairly sharp band assigned to the open chain dimer, at 3450–3440 cm^{-1}—a broader band assigned to the open chain tetramer and a very broad and strong band at 3270 cm^{-1} (shoulder at 3210 cm^{-1}) assigned to various high polymers ($n > 4$).

These assignments correlate fairly well with the bands observed here during the deuterium exchange experiments: the band at 3270 (2427) cm^{-1} is clearly the high polymer band. Similarly the band at 3570 (2650) cm^{-1} correlates with the open chain dimer and that at 2472 cm^{-1} (OD stretching only) may correspond with the open chain trimer.

Barnes and Hallam (*25*) observed no absorption bands in the region of the strong band found here at 3110 (2342 cm^{-1}). Figure 3 (C) shows that it exchanges with deuterium more rapidly than most of the other possible ethanol bands and Fig. 3 (D) shows that it is preferentially removed on heating. In view of this marked difference in behavior, we tentatively suggest that absorption in the region may reflect strong interaction between the hydroxyl groups of the ethanol and some of those inside the pores of the alumina. The band at 3488 (2580) cm^{-1} also does not fall into the groups of bands observed by Barnes and Hallam but its behavior towards deuterium and towards heating suggest a strong similarity to the very large multimer band, although no firm assignment can be made.

"Alumina" Bands

The two very large bands at ca. 1580 and 1480 cm^{-1} have until recently been thought to be intrinsic surface vibrational modes of alumina. However, Mathieu and Bozon, and Mars *et al.* (*11*) have shown independently that these bands can be removed by treatment with oxygen at 450°C. Our own results confirm this in general, because treatment with oxygen at 500°C was sufficient to remove these very intense bands almost completely. On the other hand, we found that heating to 600°C *in vacuo* would also remove them whereas Mathieu and Bozon claim that this treatment is ineffective. It is significant that Mathieu and Bozon, and Mars *et al.* (*11*) were using a nonporous microspherical γ-alumina. In the present work we have used a highly microporous gel in both the γ and the χ phases and still obtained similar absorption bands. The suggestion of Mathieu and Bozon that these are due to a surface complex involving both CO and CH_2 stretching frequencies is thus likely to be generally applicable to all aluminas.

The most recent paper on this subject (*27*) gives further details. It suggests that these bands are due to carbonate and bicarbonate species which result from oxidation of hydrocarbon contamination at the surface.

Surface Hydroxyl Groups

Our results for the behavior of the surface hydroxyl groups are almost identical to those of Peri (*8*), and are not discussed in detail here. There is the same general tendency for the stretching frequency of isolated hydroxyl groups to increase with increasing temperature of dehydration. As Dunken and Fink (*28*) have already pointed out, the γ and η phases of alumina show strikingly similar –OH frequencies (*13*); we have shown here that the γ and χ phases have also practically identical absorption frequencies. In fact, discrepancies in the published values for –OH group stretching frequencies of aluminas represent differences in dehydration conditions rather than real differences in sample constitution.

CONCLUSIONS

Infrared spectra have shown that alumina aerogels, prepared using organic liquids of low critical temperature, trap the liquid during their preparation, probably in very narrow micropores. Alcohol-prepared aluminas alone can retain carbon dioxide formed by oxidation of the pyrolyzed organic material, after heating in air or oxygen to 600°C. The other aerogels allow the carbon dioxide produced in this way to diffuse away.

The shape and position of the infrared bands of all trapped molecules of both the original organic compounds and of the carbon dioxide suggest strongly that they are present in a condensed state. Trapped ethanol is particularly interesting, because it shows evidence of very strong hydrogen bonding between the alcohol molecules (just as it does when ethanol is in the liquid state) and also a band possibly due to hydrogen bonding between one ethanol molecule and the alumina surface.

No evidence was found of chemisorption either of carbon dioxide or of ethanol on the alumina, although both these compounds normally give well-defined infrared spectra on adsorption (*29*, *30*).

It is not possible to make quantitative statements about the reason for this behavior on the evidence of the infrared spectra alone, but we can propose a tentative hypothesis to account for the main features of the observed spectra. Alumina gels are known to be highly microporous, the dimensions of the smallest pores being comparable to those of the nitrogen molecule (*31*). In the gels under study here it is most likely that the relatively bulky organic molecules are at least partially sealed-off by constrictions of about 4–5 Å diameter in the autoclaving process. The constrictions must be large enough (or become large enough) to admit oxygen, because carbon dioxide is formed by heating the gels in oxygen even after prior heating *in vacuo* to decompose the organic compound. Similarly, in alcohol-prepared aerogels, deuterium must be able to diffuse in to exchange with the alcoholic –OH groups. Carbon dioxide, on the other hand, is just too big to diffuse out, although gels prepared from ether and other large molecules do allow it to disperse.

In Part II of this series, we shall examine this preliminary hypothesis to see whether it is confirmed by evidence from methods which have been recently developed to determine the surface texture of microporous solids, and to see whether we can account for the difference between the alcohol- and ether-prepared aerogels.

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