

Molecules trapped in Micropores of Alumina Aerogels

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ALUMINA aerogels made by the method of Peri and Hannan¹ (by the use of Kistler's technique² of removing ethanol above its critical temperature, 240°, from the alumina alcogel and calcination in air at 600°), generally have an i.r. band at *ca.* 2340 cm.⁻¹ which has been attributed to carbon dioxide trapped in sealed-off pores.³ Neither heating of the alcogel under reduced pressure, to 1000°, nor subsequent chemisorption of adsorbates affects this band. A typical sample gave the band centre at 2346 ± 2 cm.⁻¹, the absorbance (*A*) as 0.12 cm.⁻¹, and $\Delta\nu_{\frac{1}{2}}$ as 18 cm.⁻¹ (a Grubb Parsons GS2 grating spectrometer was used). No spectrum of liquid carbon dioxide has been published, but there was a much closer resemblance to the solid-state band (band centre, 2342 cm.⁻¹) $\Delta\nu_{\frac{1}{2}}$ 8.0 cm.⁻¹, *A*, 1.35)⁴ than to the gaseous.

The carbon dioxide was shown to originate from the ethanol used in the preparation of the aerogel by measuring the i.r. spectra (at 100° intervals from 200 to 900°) of uncalcined specimens taken straight from the autoclave. These showed broad bands at 3100 and 3280 cm.⁻¹ (hydrogen bonded OH groups; *cf.* OH band in ethanol at 3300 cm.⁻¹)⁵

and strong bands in the region 2850—2950 cm.⁻¹ (C-H) superimposed on the broad bands of the OH groups of the alumina. The bands due to ethanol were removed when the specimen was heated at 500°, a small band in the region 3040—3060 cm.⁻¹ indicated the presence of unsaturated hydrocarbons. The band due to carbon dioxide appeared only when the sample was heated in oxygen, and then only at 600°.

Preparation of the aerogel by immersion of the alcogel in liquid diethyl ether, followed by heating of the specimen above the critical temperature of the ether (220°), gave samples which showed no carbon dioxide band after calcination in oxygen at $\geq 600^\circ$. Spectra of uncalcined samples showed that the ether was held in a similar manner to the ethanol in the ethanol-prepared aerogels, but no broad OH bands other than those of alumina were observed.

Since it seemed likely that the band at 2346 cm.⁻¹ was due to carbon dioxide formed by the reaction of oxygen with carbonaceous residues from the pyrolysis of ethanol and trapped in narrow micropores, we investigated the surface

texture of the alcohol- and ether-prepared aerogels in an attempt to determine why the latter did not trap the carbon dioxide. A Cahn RG vacuum "Electrobalance" was used to measure adsorption isotherms for nitrogen at -196° and for carbon tetrachloride at 20° , the aerogels being thermally treated exactly as in the i.r. studies. t -Plots⁶ and " v_g "-plots⁷ were derived from the results to see whether the two aerogels had different micropore structures. Micropore volumes in particular were calculated from the " v_g " plots by the method of Sing.⁸ The Figure shows the micropore volumes of the two aerogels after calcination as determined with the use of nitrogen (molecular diameter, 4.3 \AA)⁶ and carbon tetrachloride (6.2 \AA).⁹

These results clearly indicate that the ether-prepared aerogel has, for all calcination temperatures, much the higher micropore volume accessible to nitrogen (curve A) although most of this is not accessible to carbon tetrachloride (curve A'). Furthermore, in contrast to the behavior of the alcohol-prepared aerogel, whereas there is a decrease with increasing temperature of the micropore volume accessible to nitrogen, there is an increase between 300° and 500° of that accessible to carbon tetrachloride, indicating that at least some of the smaller micropores are opened up on heating. This is not a result of phase changes, since the volumes of micropores accessible to nitrogen (curve A) show a steady decrease due to sintering.

Both the i.r. and the adsorption results are consistent with a model where the ether or alcohol is trapped in narrow micropores (*ca.* between $4\text{--}8 \text{ \AA}$ in diam.) in a quasi-liquid state. Pyrolysis occurs with the formation of carbonaceous residues; the other possible products, water and hydrogen will escape by diffusion through the pores. Above 500° , reaction with oxygen will occur, but the majority of the micropores in the alcohol-containing gel are of sufficiently low diameter to prevent carbon dioxide (maximum diam. 5.23 \AA)¹⁰ from escaping, whereas the micropores in the ether-containing gel are large enough to allow diffusion.

The details of this model are at present not clear, but it seems likely that any method for making microporous gels by the use of organic compounds might lead to a similar trapping effect.

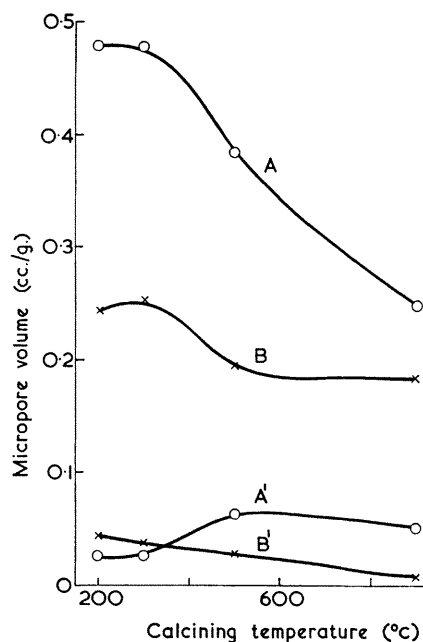


FIGURE. Variation of micropore volumes of alumina aerogels with degassing temperature. Upper curves, (A and B) as determined with nitrogen; lower curves (A' and B') as determined with carbon tetrachloride. \circ Ether-prepared aerogel, \times alcohol-prepared aerogel.

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¹ J. B. Peri and R. B. Hannan, *Spectrochim. Acta*, 1960, **16**, 237.

² S. S. Kistler, *J. Phys. Chem.*, 1932, **36**, 52.

³ J. B. Peri, *J. Phys. Chem.*, 1965, **69**, 211.

⁴ H. Yamada and W. B. Person, *J. Chem. Phys.*, 1964, **41**, 2478.

⁵ Documentation of Molecular Spectroscopy, Butterworth, card No. 3777.

⁶ B. C. Lippens, and J. H. de Boer, *J. Catalysis.*, 1965, **4**, 319.

⁷ K. S. W. Sing, *Chem. and Ind.*, 1968, 1520.

⁸ K. S. W. Sing, *Chem. and Ind.*, 1967, 829.

⁹ N. N. Augul', A. V. Kiselev, I. A. Lygina, and E. A. Mikhailova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1962, **5**, 769.

¹⁰ R. M. Hexter and T. D. Goldfarb, *J. Inorg. Nuclear Chem.*, 1957, **4**, 171.