JOURNAL OF CHROMATOGRAPHY

CHROM. 5819

SURFACE-MODIFIED ALUMINA FOR HYDROCARBON SEPARATIONS

M. G. NEUMANN AND W. HERTL
Facultad de Ciencias, Departamento de Química, Universidad de los Andes, Mérida (Venezuela)

(Received October 19th, 1971)

SUMMARY

A parallel infrared spectroscopic–gas chromatographic study was undertaken in which three representative compounds, an alcohol, pyridine and an acid anhydride, were used to partially deactivate an alumina support material. The most active sites on an alumina surface, which lead to severe tailing and excessive retention times, are the electron-accepting aluminum atoms. These sites can be effectively removed by treating the alumina with pyridine or an acid anhydride, and lead to greatly improved resolution in hydrocarbon analyses. The *in situ* method of treating the support material in the chromatograph is simple and rapid. By using a chemical reaction for the deactivation only the most active undesirable sites are removed. These methods are independent of the support surface area and of the amount of reagent used for the treatment.

INTRODUCTION

Alumina can be used as a support material in gas–solid chromatography (GSC) for hydrocarbon analyses, particularly when one wishes to separate various isomers of a given hydrocarbon or members of a homologous series with similar boiling points. When separating compounds of this type it is necessary to strike a balance between having surface sites which are sufficiently active to achieve the separation, but not so active as to retain the adsorbates excessively, thus giving rise to long retention times and severe tailing of the chromatographic peaks.

Alumina has a very active surface, and for GSC purposes can be partially deactivated with silicone oil[1], water[1] or inorganic salts[2–4]. Although the incorporation of alkali into alumina[5] has been reported to poison the strong acid sites, thus preventing isomerization of cyclohexene, it is not clear from the conditions used for treating the chromatographic supports with salts (*i.e.* deposition which leaves 10% by weight on the alumina) whether the main effect is due to ion exchange with the alumina surface or to a complete salt coating.

In order to devise surface treatments so as to effect better separations, one should know exactly what happens on the alumina surface as a result of deactivation.

To this end, a parallel chromatographic and spectroscopic study was undertaken, in which three representative types of compound (alcohol, pyridine and a carboxylate compound) were used for deactivation.

Alumina has a complex surface. Numerous studies[6,7] of its surface properties have been carried out, particularly by IR techniques, in order to study its catalytic properties. The active sites on an alumina surface are: (a) Three, or five, types of hydroxyl group, the type being determined by the number of nearest oxide neighbors. Three of these types are distinguishable spectroscopically and they show slightly different reactivities. (b) The Lewis acid (electron-accepting) sites which are due to aluminum ions attached to three oxygen atoms. (c) The oxide ions.

If one adds a proton to a Lewis acid, one obtains a Brønsted acid; however, there is no evidence that this takes place on alumina, at least in so far as strong protonic sites are concerned. From catalytic studies, it is generally agreed that the Lewis acid sites are the most active surface sites on alumina. These acid sites are thought to arise when the hydroxyl groups condense and eliminate water, at temperatures above 400°, leaving oxide ions and vacancies on the surface; if two vacancies are adjacent, an aluminum ion is exposed and this is a Lewis acid.

These Lewis acid sites can adsorb molecules in several ways. Ketones, for example, form stable complexes with the Lewis acid sites via the oxygen atom of the carbonyl group. The acceptance of the electrons on the oxygen atom into the vacant orbital of the Lewis acid causes a lowering in the IR absorption frequency of the carbonyl group. Olefinic groups[8,9] adsorb as a π-complex with the electron-deficient Lewis acid sites.

Pyridine and amines readily adsorb on an alumina surface. Physically adsorbed pyridine desorbs at temperatures above 150°, leaving pyridine coordinated to surface Lewis acid sites. This coordinated pyridine gives rise to IR absorption bands at 1453 and 1457 cm^{-1}. The appearance of two bands is apparently due to two distributions of Lewis acid sites with different acid strengths. Pyridine, being a weak base, reacts only with the stronger acid sites[6].

Methyl alcohol reacts with an alumina surface at low temperatures to produce surface methoxide groups[10]; on heating above 170° the methoxide group is oxidized to a surface formate group. This oxidation is probably due to the Lewis acids.

Many other reactions between various adsorbates and alumina are reported in the literature, but these few examples illustrate the possibility of selective chemisorption on the known undesirable surface sites in order to obtain better chromatographic separations.

EXPERIMENTAL

Spectroscopy

All spectra were recorded with a Perkin-Elmer Model 621 IR spectrophotometer. The alumina samples were prepared by pressing a self-supporting disc of high area alumina (Alon C, surface area approx. 90 m^2/g) at 24 000 p.s.i. in a 1-in.-diameter circular die. The alumina disc was mounted in a vacuum-tight furnace fitted with IR transmitting windows. This furnace with the alumina sample was mounted in the spectrophotometer and the furnace connected to a conventional high-vacuum rack.

The surface treatment of the alumina consisted of raising the temperature of the furnace containing the alumina sample, evacuating it, and adding the vapor of the desired reagent to the furnace. After a period of time, the furnace was again evacuated and a spectrum taken to determine what species were bonded to the alumina surface. The exact conditions are given with the data.

Chromatography

The alumina support material (Alcoa type F-1 chromatography grade, screen size 60/80) was evaluated in a Varian Aerograph Model 1860 gas chromatograph, using flame ionization detectors. The alumina was packed in 1/4-in.-O.D. aluminum columns with a length of 80 cm. The columns were pre-conditioned for 3 h at 400° with a nitrogen flow of 40 ml/min. A Hamilton 1-µl syringe was used to deliver the liquid samples. The operating conditions are given with the data. Since the object of this study was to determine specific interaction effects with the alumina support, no attempt was made to obtain optimum operating parameters with the chromatograph.

Surface treatment of the chromatographic alumina

All the surface treatments of the alumina support were carried out *in situ* in the chromatograph. Twenty to thirty aliquots of 5 µl were injected into the column at the following column temperatures: *n*-butanol 400°, acetic anydride 400°, pyridine 250°. After all the excess reagent had passed through the column, as determined by the detector response, the column temperature was reduced to operating temperature and the evaluation experiments were carried out. The treated alumina supports were evaluated by obtaining chromatograms of a series of standard hydrocarbons and also of a sample of commercial gasoline.

In a previous study of this type, using Chromosorb 102 (ref. 11) as a column support, it was possible to predict, on the basis of the spectroscopic experiments, which adsorbates would lead to excessive retention and tailing. This was not possible in this study, since the physical adsorption properties of the alumina used in the spectroscopic study might reasonably be expected to differ from that of the alumina used in the chromatographic column, the particle sizes differing considerably. The chemical properties of the aluminas, however, should be the same in both cases.

RESULTS AND DISCUSSION

Fig. 1 shows the spectra of alumina taken in air at various temperatures between 30° and 400°. The large band in the spectra is due to adsorbed water. Clearly the amount of water on the surface varies greatly with the temperature. On lowering the temperature in air, water is readsorbed on the surface.

The spectra of the alumina before and after having been exposed to *n*-butanol vapor at 250° are given in Fig. 2. After exposure there is a small decrease in the intensity of the Al–OH band(s) near 3720 cm^{-1}; C–H stretching bands due to the chemisorbed butanol appear in the region 2800–3000 cm^{-1} (Fig. 2a), and bands appear at 1460 and 1560 cm^{-1} (Fig. 2b). These latter two bands arise due to oxidation of the alcohol group of the butanol to produce a carboxylate group bonded to the surface[10].

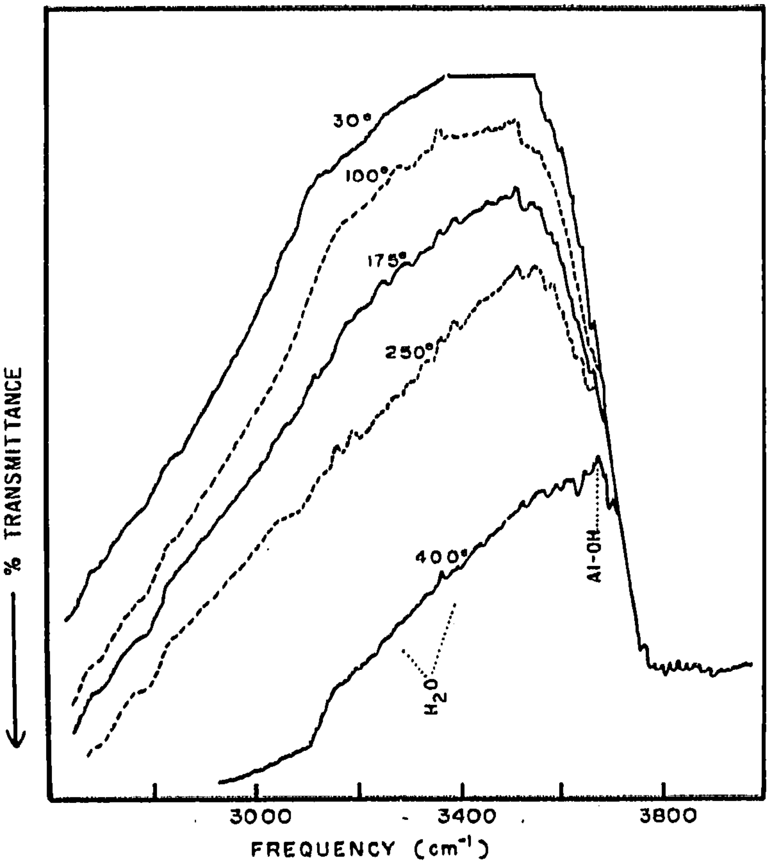


Fig. 1. Spectra of alumina heated in air to various temperatures, showing removal of adsorbed water.

This is discussed below. The same spectra were obtained initially on another alumina sample when the butanol was added at 400°.

Exposure of this treated alumina to water vapor at 200° for 1 h resulted in no significant changes in the intensities of the C–H or C=O bands, although water did readsorb on the surface. Thus, the bonded species is stable with respect to hydrolysis. On exposure to air at 250° there was a slow but steady decrease in the intensities of the C–H bands, due to oxidation of the hydrocarbon chain; the bonded C=O groups showed no change.

When pyridine binds by coordination to the Lewis acid sites on alumina, characteristic bands appear at 1453 and 1457 cm^{-1}. Since this is well documented in the literature[6,7], the spectrum is not reproduced here. When pyridine was added to the butanol-treated surface at 400° strong bands appeared at 1445 and near 1570–1600 cm^{-1} (Fig. 2b). The exact frequencies are difficult to determine owing to the overlap between the strong C=O and pyridine bands. Although these observed frequencies are nearer to those usually observed when pyridine is physically adsorbed, the pyridine must be chemisorbed, since it is fairly stable at 400° *in vacuo*. Concurrent with the addition of the pyridine there is a frequency shift of the C=O band at 1460 cm^{-1} (*cf.* Fig. 2b), showing that there is an interaction between the pyridine and the surface C=O groups. The results from the chromatographic study, described below, show that there are Lewis acid sites still available after treatment with

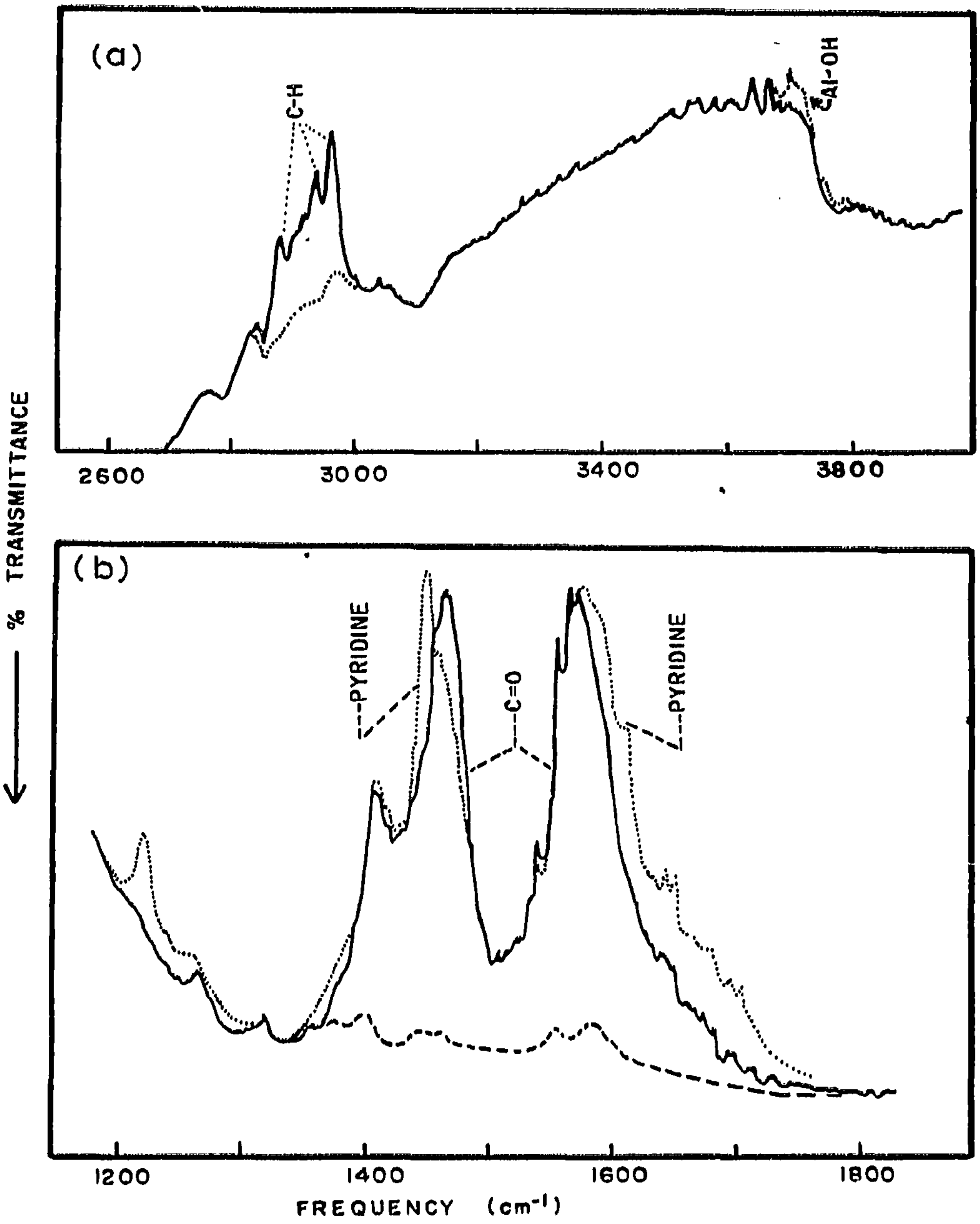


Fig. 2. (a) Spectra before (dotted line) and after (solid line) reaction with 5 torr *n*-butanol at 250° for 1 h. (b) Spectra before (dashed line) and after (solid line) reaction with *n*-butanol. 3 torr pyridine added and evacuated (dotted line) at 400°.

butanol, so that these bands must arise from the pyridine which complexes both to the C=O groups and to the Lewis acid sites.

When acetic anhydride reacts with a fresh alumina surface at 400° (*cf.* Fig. 3) a large decrease in the amount of adsorbed water is observed and two strong bands appear at 1465 and 1585 cm^{-1}. These two bands are due to the symmetric and asymmetric stretching frequencies of the carboxylate C=O, and are near, but not identical, in frequency to the bands observed when butanol was reacted with the alumina. Although acid anhydrides show a typical doublet C=O band (at 1824 and 1748 cm^{-1} in the case of acetic anhydride) it is more likely that the acetic anhydride was hy-

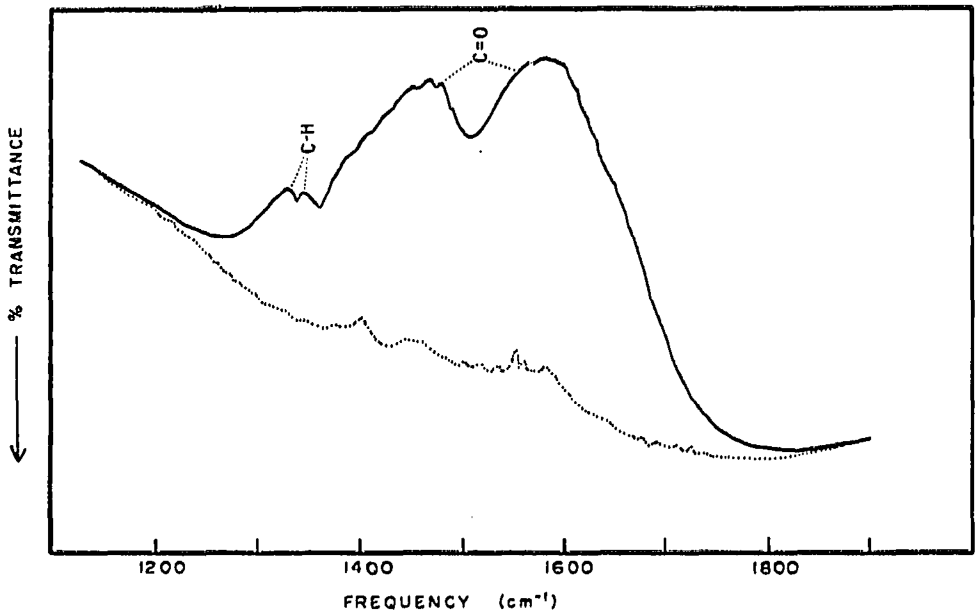


Fig. 3. Spectra of alumina at 400° (dotted line) and after reaction (solid line) with five aliquots of 3 torr acetic anhydride for 25 min total.

drolyzed prior to its reaction with the surface, since a decrease in the quantity of adsorbed water was observed and the separation of the C=O bands was about 120 cm^{-1} after the acid had reacted. On addition of pyridine to the acid-treated surface, bands appeared near 1450 and 1600 cm^{-1} due to a pyridine/C=O complex.

TABLE I

RETENTION TIMES OF STANDARD HYDROCARBONS ON UNTREATED AND TREATED ALUMINA COLUMNS

Column temperatures: *n*-Butanol-treated column and its reference untreated column, 150°; all others (below dotted line), 200°. 0.2 µl of each compound was injected using a nitrogen flow of 40 ml/min.

Compound	*Retention times on alumina columns*				
	Untreated	*n-Butanol-treated*	*Pyridine-treated*	*Pyridine-treated and heated to 400°*	*Acetic anhydride-treated*
n-Hexane	3.1	3.1			
n-Heptane	6.0	5.8			
n-Octane	12.2	11.5			
Acetone	36.0	35.5			
Benzene	7.7	7.2			
Benzene	6.0		5.6	5.0	5.0
Toluene	13.6		12.4	12.2	10.8
m-Xylene	29.2		26.4	26.4	22.3
o-Xylene	34.4		31.2	32.2	27.1
p-Cymene	93.6		85.2	96.0	79.2
Pentene	1.4		1.4	1.7	1.4
Hexene	3.1		3.1	3.6	2.9
Heptene	6.0		6.0	7.0	5.5
Octene	14.2		13.7	16.6	12.5
n-Nonene-1	32.9		30.2	>250	27.6

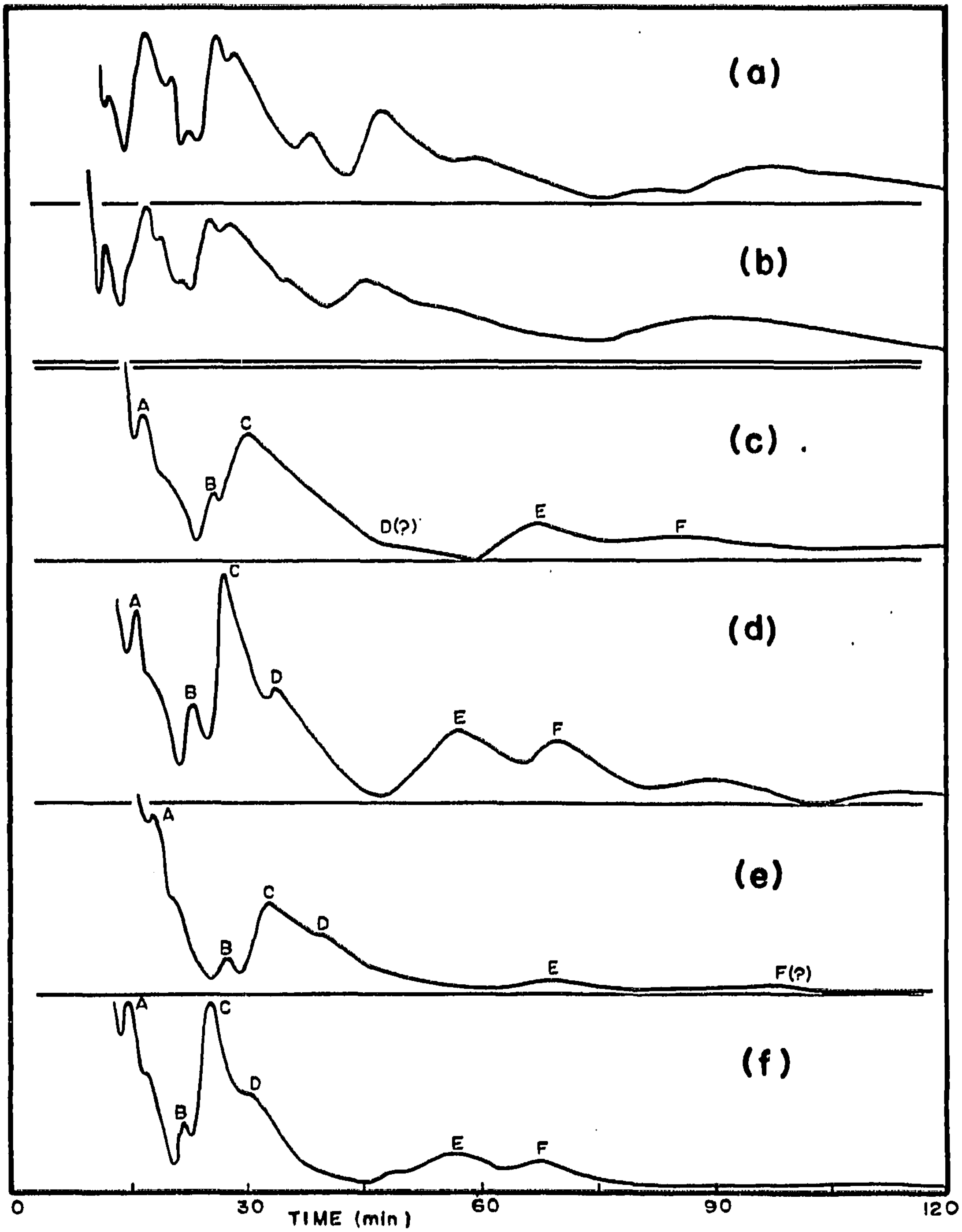


Fig. 4. Gas chromatograms of a commercial gasoline obtained on alumina supports: (a) untreated alumina, (b) *n*-butanol-treated alumina, (c) untreated alumina, (d) pyridine-treated alumina, (e) same as (d), but column raised to 400° for 2 h and then returned to 200°, (f) acetic anhydride-treated alumina. Column temperatures: 240° for (a) and (b), 200° for (c), (d), (e) and (f). 1-μl samples of gasoline were used with a nitrogen flow of 40 ml/min. The peaks for the lighter fractions of the gasoline which were eluted within the first 10 min are not reproduced on the chromatograms, since they were all virtually identical, regardless of the surface treatment.

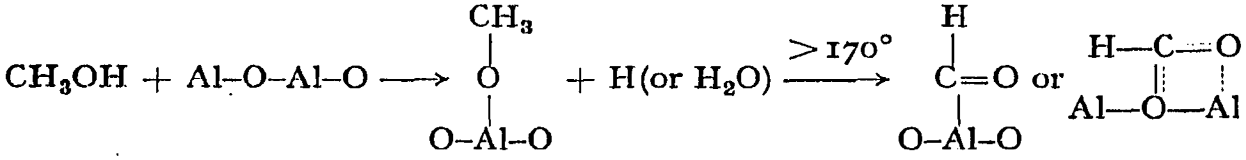
With this information on the surface reactions, one can now consider whether any of these surface treatments lead to improved column performance. The retention times of the reference hydrocarbons on the untreated and treated alumina columns are given in Table I. For illustrative purposes, chromatograms of a commercial gasoline, analyzed on the same columns, are given in Fig. 4. Comparison of the data in Table I and the chromatograms in Fig. 4 shows clearly that the butanol-treated surface is not significantly different in its separation properties from untreated alumina. Furthermore, after about 100 h of operation at 170°, a positive baseline drift appeared on the response of the treated column. This is probably due to decomposition of the hydrocarbon chain.

Several columns were treated with *n*-butanol using research grade argon in order to determine if traces of water vapor or oxygen in the nitrogen carrier gas were causing decomposition of the bonded butanol. No differences were noted in the chromatograms obtained, indicating that the decomposition of the hydrocarbon chain is probably due to thermal pyrolysis.

The pyridine- and acetic anhydride-treated supports lead to improved separations and shorter retention times with improved peak shapes (*cf.* Fig. 4 and Table I). Clearly the surface bonding sites for pyridine and acetic anhydride are different from the bonding sites for butanol.

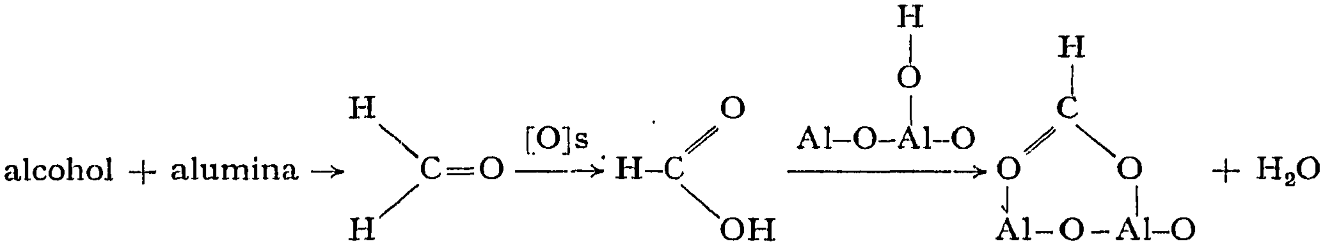
Pyridine was applied to the column at 250° and yielded good results. The column temperature was raised to 400° for 2 h and then returned to 200°. The chromatograms obtained from this column were very poor. Note particularly that *n*-nonene-1 (Table I) required more than 250 min to be eluted, compared with 33 min on the untreated column. This was repeated three times and the same effect was observed. The degeneration of the column is probably due to traces of oxygen in the carrier gas, leading to oxidation of the pyridine, since the spectroscopic experiments showed that the bonded pyridine is stable at 400° *in vacuo*. Why the nonene should be excessively retained on this degraded column is not clear.

Using these spectroscopic data in conjunction with the chromatographic data, the chemistry of these surface reactions can be considered. To summarize, butanol binds to the surface and the alcohol group is oxidized to a carboxylate group, but does not react with the Lewis acid sites; acetic anhydride (or the acid) and pyridine bind to the surface and remove most of the Lewis acid sites. How the acids and alcohols react with the alumina surface has not been completely resolved, but the following tentative schemes have been proposed. GREENLER[10] suggested that:



$$CH_3OH + Al\text{-}O\text{-}Al\text{-}O \longrightarrow \underset{O\text{-}Al\text{-}O}{\overset{CH_3}{O}} + H(\text{or } H_2O) \xrightarrow{>170^\circ} \underset{O\text{-}Al\text{-}O}{\overset{H}{C{=}O}} \text{ or } \begin{array}{c} H\text{—}C\text{=}O \\ Al\text{—}O\text{—}Al \end{array}$$

CHAPMAN AND HAIR[6,12] found that when aldehydes and alcohols react with alumina, both produce surface carboxylate groups similar to the acid; in the case of alcohol hydrogen was produced, whereas in the case of aldehyde no hydrogen was produced. According to them the following reactions took place:



Comparing these two reaction schemes with the chromatographic data strongly suggests that in the case of the alcohol reaction followed by oxidation, the C=O groups are bonded principally to the O atoms of the alumina surface; in the direct acid reaction, the bonding is principally to the surface aluminum atoms, thus effectively removing most of the Lewis acid sites. Both proposed schemes may be correct, but the bonding sites are different for alcohols and acids.

CONCLUSIONS

The most active surface sites on alumina which lead to severe tailing and long retention are the Lewis acid sites (electron-attracting aluminum atoms). By removing these sites one can attain a satisfactory compromise between effective separation of hydrocarbons and reasonable retention times. The advantages of this treatment over deposition methods or the reversible adsorption of water are: (i) the chemical reaction methods are independent of the support surface area and the amount of reagent used for treatment; (ii) only the most active sites are removed or blocked; and (iii) the *in situ* method of treating the alumina in the chromatograph is simple and rapid.

ACKNOWLEDGEMENT

The gift of the Alon C alumina by Cabot Co., Boston, is gratefully acknowledged.

REFERENCES

1 C. G. Scott, *J. Inst. Petrol.*, 45 (1959) 118.
2 C. G. Scott, *Gas Chromatography 1962*, Butterworths, Washington, 1962, p. 36.
3 C. G. Scott and C. S. G. Phillips, *Gas Chromatography 1964*, Institute of Petroleum, London, 1965, p. 266.
4 D. J. Brookman and D. T. Sawyer, *Anal. Chem.*, 40 (1968) 106.
5 H. Pines and W. O. Haag, *J. Amer. Chem. Soc.*, 82 (1960) 2471.
6 M. L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, New York, 1967, pp. 141ff.
7 L. H. Little, *Infrared Spectra of Adsorbed Species*, Academic Press, London, 1966, pp. 180ff.
8 J. B. Peri, *Proceedings of the Third International Congress on Catalysis*, North-Holland, Amsterdam, 1965, p. 654.
9 L. H. Little, H. E. Klauser and C. H. Amberg, *Can. J. Chem.*, 39 (1961) 42.
10 R. G. Greenler, *J. Chem. Phys.*, 37 (1962) 2094.
11 W. Hertl and M. G. Neumann, *J. Chromatogr.*, 60 (1971) 319.
12 I. D. Chapman and M. L. Hair, *Proceedings of the Third International Congress on Catalysis*, North-Holland, Amsterdam, 1965, p. 1091.