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RELATIONSHIP BETWEEN CHROMATOGRAPHIC PERFORMANCE AND SURFACE STRUCTURE OF ALUMINA MICROSPHERES[*]

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SUMMARY

Spherical alumina high-performance liquid chromatography packing material has been thermally modified at temperatures ranging from 200 to 950°. The chromatographic performance of the modified columns was tested using solutes of varying column capacity ratio ($k' = 0$–14), with *n*-hexane as the eluent. The parameters k', α, and φ' have been obtained and conclusions concerning the solute adsorption mechanisms at various temperatures have been postulated.

The effects of pre-treatment of the alumina on the column characteristics prior to column packing are also discussed.

INTRODUCTION

Following a recent investigation of Spherisorb silica high-performance liquid chromatographic (HPLC) packing material[1], the present work was an attempt to apply the same experimental techniques to Spherisorb alumina HPLC packing material, with the intention of providing further data for the possible prediction of chromatographic separations.

Alumina has always taken a secondary role to silica as a liquid chromatographic packing material, possibly owing to the greater difficulty in understanding the complex adsorption mechanisms.

Before any adsorption mechanism could be proposed, a knowledge of the alumina surface structure is essential, as was found with silica[1,2]. Analytical techniques, such as infrared spectroscopy[3–7], chemical modification[3,6,8] and thermogravimetric analysis (TGA)[4,8,9], have been used to elucidate several postulations concerning the surface structure of alumina.

Most workers[6,8,10] now agree that the surface of γ-alumina (a low-temperature crystalline form of alumina[11]) consists of a layer of oxide ions (O^{2-}) with aluminium ions (Al^{3+}) forming the penultimate layer[12]. The ions are arranged as in a defect spinel structure in which stoichiometry demands distortion of the normal spinel structure, causing surface site vacancies[11]. The surface vacancies cause the surface to be highly active; thus water coverage is common, mainly in the form of physisorbed water. The degree of surface coverage by the water controls the surface activity and thus the adsorption properties. Different temperatures have been reported for the complete removal of the molecular water[7,11,13,14].

A mixture of the individual theories that seems to give the best approximation of the model for adsorption on alumina has been presented[6,8,10]. Such a model incorporates the following types of adsorption site:
  (1) the surface hydroxyl groups[15,16];
  (2) the oxide ions (O^{2-});
  (3) the aluminium ions (Al^{3+}, the Lewis acids)[17];
  (4) the vacant sites formed by the removal of the coordinated hydroxyl groups[8].

The object of the present study was to examine chromatographically the alumina surface adsorption properties at temperatures ranging from 200 to 950°, where the alumina surface passes through several stages of molecular water and hydroxyl group coverage[2].

During the course of the investigation, the flow resistance parameter (φ) was measured in order to measure the effect of the thermal treatment on the porosity of the packed alumina column.

EXPERIMENTAL

The liquid chromatograph consisted of the same system as previously described[1], which incorporates a coil-pump, for constant-pressure solvent delivery, and a Cecil (Cambridge, Great Britain) Model CE 212 UV spectrometric detector.

The alumina adsorbent was taken from a 100-g batch of Spherisorb ALOY, which had the following physical characteristics: surface area, 95 m^2/g; pore volume, 0.36 cm^3/g; average pore diameter, 134 Å. The Spherisorb alumina was used directly from the manufacturer's container without further treatment.

The alumina ALOY was slurry packed into a 10.6 cm × 4 mm I.D. stainless-steel column, using the procedure described previously[1,2]. The packed column was connected via a loop injector to the coil-pump. The mobile phase, n-hexane, was introduced into the column and passed through the packed column until the slurrying solvent (methanol) was removed and complete equilibration was achieved as indicated by a steady recorder baseline.

The following solutes were placed on the column in order to evaluate the column parameters (k', α and φ')[1]: n-pentane (t_0), o-xylene, m-xylene, p-xylene and nitrobenzene. The chromatograms were recorded for duplicate runs at each of the following mobile phase flow-rates: 1.5, 2.0, 2.5 and 3.0 ml/min. After the initial evaluation of the column parameters, the column (with nitrogen gas passing through it) was placed in an oven at 120° for 1 h in order to remove the mobile phase. While continuing the nitrogen flow, the Spherisorb alumina ALOY column was placed in a tube furnace, accurately maintained at 200°, for 2 h. The column was the removed,

cooled and the column parameters were re-evaluated with the same mobile phase–solute system. The column was returned to the 120° oven for 1 h (to remove the *n*-hexane), then heated in the furnace at the next temperature for 2 h.

The temperatures used were 200, 300, 400, 500, 600, 750, 900 and 950°. The results obtained are the average of results from two Spherisorb alumina ALOY columns in each instance.

TGA measurements were made on small batches of Spherisorb alumina ALOY, heated at the same temperatures for 2 h in a nitrogen atmosphere. The measurements were made on a Stanton Redcroft HT-D thermobalance, by heating the samples from constant weight at 200° to constant weight at 1100° and recording the weight loss. The weight loss was due to the removal of the total surface water.

RESULTS AND DISCUSSION

In Fig. 1, the decrease in hydroxyl content with an increase in temperature is shown; a steady decrease in the amount of surface water can be seen over the temperature range 200–1100°. The total surface hydroxyl group concentration for Spherisorb alumina ALOY is shown to be approximately three times that for Spherisorb silica SLOW (*i.e.*, $n_{OH} = 4.6$ OH per 100 Å²)[1]. This is due to the higher activity of the alumina surface, which has been shown to be more active than silica towards water adsorption[14]. The higher surface hydroxyl group concentration also explains why the molecular water is removed at 200° and not at 120°, as was the case for Spherisorb silica SLOW (shown by differential thermal analysis)[2]. The higher the concentration of the hydroxyl groups, the more difficult it is to remove completely the surface molecular water.

The column adsorption parameters (k', α and φ') of thermally modified Spheri-
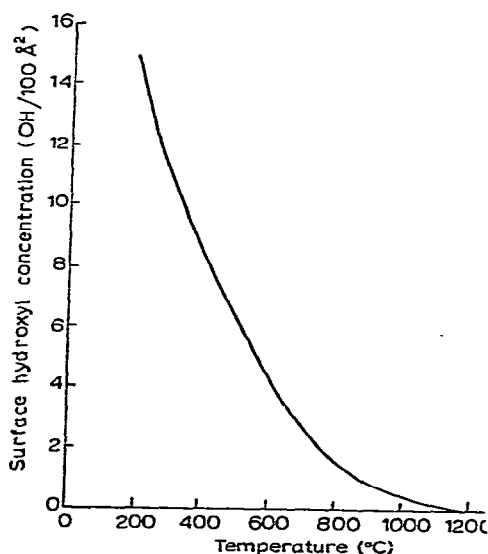

Fig. 1. Effect of temperature on the surface hydroxyl concentration of Spherisorb ALOY alumina.

sorb alumina ALOY were calculated using the techniques and equations described previously[1]. The results are presented in Table I and, for further clarity, the parameters are plotted against the temperature of heating in Figs. 2 and 3.

TABLE I

PARAMETERS OBTAINED FROM CHROMATOGRAMS FOR THERMALLY MODIFIED SPHERISORB ALUMINA ALOY

Temperature (°C)	Parameter	Compound				
		o-Xylene	m-Xylene	p-Xylene	Impurity	Nitrobenzene
25	k'	—	0.28	—	—	2.05
	α					
	φ'			821		
200	k'	1.05	1.47	1.88	2.16	3.04
	α		1.4	1.28	1.15	1.41
	φ'			798.5		
300	k'	1.26	2.0	2.32	2.64	4.11
	α		1.59	1.16	1.14	1.56
	φ'			765		
400	k'	1.35	2.24	2.67	3.43	5.92
	α		1.66	1.19	1.28	1.73
	φ'			7.33		
500	k'	1.61	2.91	3.31	4.38	8.22
	α		1.8	1.14	1.32	1.88
	φ'			737		
600	k'	1.78	3.8	4.72	7.47	11.05
	α		2.13	1.24	1.58	1.48
	φ'			744		
750	k'	1.64	4.35	7.5	12.1	14.15
	α		2.65	1.72	1.61	1.17
	φ'			764		
900	k'	0.9	1.8	3.46	5.9	7.6
	α		2.0	1.92	1.71	1.29
	φ'			697		
950	k'	0.91	1.01	2.57	3.0	3.7
	α		1.11	2.54	1.17	1.23
	φ'			7.05		

Fig. 2 is a plot of the column capacity ratio (k') against the heating temperature for Spherisorb alumina ALOY. The k' values increase to a maximal value of approximately 14 at 650–750°. Between 750° and 900°, the k' values decrease rapidly to values similar to those obtained at 200°.

The experimentally observed increase in the k' values has been found by other workers[12,17–20], and can possibly be explained in the following manner.

Heating to 300° causes the removal of molecular water from the alumina, with the formation of surface hydroxyl groups and Lewis acid centres[4,11,21]. Further heating (300–600°) causes the removal of the adjacent hydroxyl groups with the formation
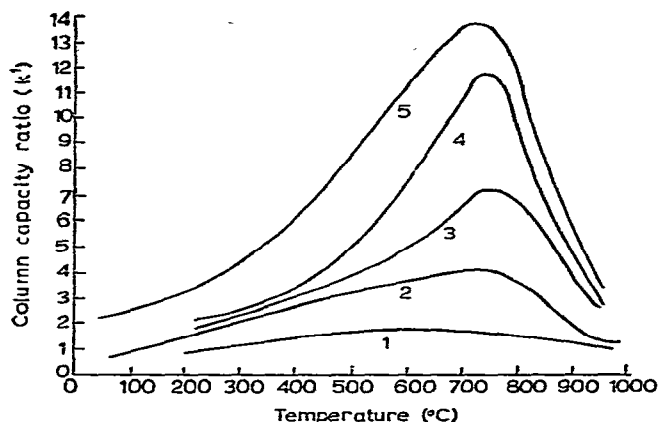
Fig. 2. Effect of temperature on the column capacity ratio (k'). Components: 1 = o-xylene, 2 = m-xylene, 3 = p-xylene, 4 = impurity, and 5 = nitrobenzene.

of more strong Lewis acid sites on the surface[4]. Thus, the k' values increase with temperature. The k' values decrease when the surface area begins to be affected, and decrease rapidly above 900°.

The results in Fig. 2 agree with those of previous work[8,12,17,22], where the surface hydroxyl groups were considered to be unimportant in the adsorption process and the major adsorption sites were attributed to the exposed aluminium ions (Al^{3+}) acting as Lewis acids.

Comparing the results for Spherisorb alumina ALOY and Spherisorb silica SLOW[1], it can be seen that adsorption mechanism predictions are simpler on the silica, the active sites being the surface hydroxyl groups, whose concentration is simple to control. Also, the higher activity of the Spherisorb alumina indicates that more molecular water is retained on the surface (as shown by the TGA results, and therefore a pre-drying temperature of 400° is suggested.

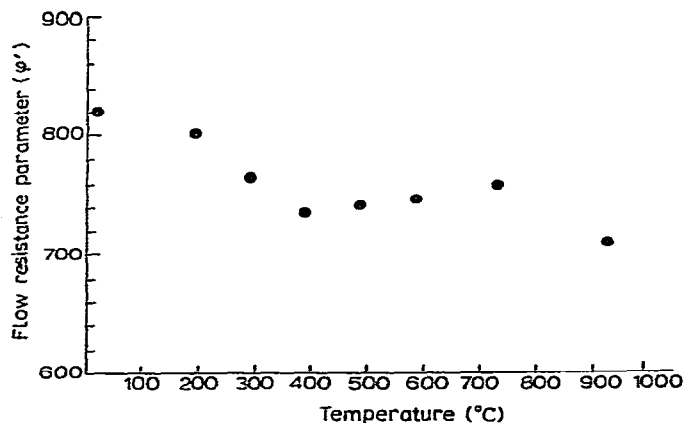Fig. 3 is a plot of the flow resistance parameter (φ') against the heating tem-

Fig. 3. Effect of temperature on the flow resistance parameter (φ').

perature for Spherisorb alumina ALOY. The φ' values decrease slightly over the range 100–900°. Therefore, it can be assumed that as a constant value for φ' indicates a regular packed bed structure[22,23], the increase in the heating temperature does not affect the packing structure.

CONCLUSION

It can be concluded that Spherisorb alumina ALOY has the characteristic properties expected of a γ-alumina. The adsorption mechanism probably involves the aluminium ions acting as Lewis acids, in an electrostatic manner. The surface hydroxyl groups are thought to be unimportant in the adsorption process.

Study of the flow resistance parameter (φ') at various temperatures showed that the alumina packed bed is almost unaffected up to 900°.

Pre-treatment of the Spherisorb alumina ALOY at 400° prior to slurrypacking is suggested.

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