CHARACTERIZATION OF MODIFIED ALUMINA AS AN ADSORBENT FOR GAS–SOLID CHROMATOGRAPHY

MODIFICATION WITH AMMONIUM FLUORIDE

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SUMMARY

Modification of the adsorptivity of alumina by coating it with ammonium fluoride, with thermal treatment before and after coating, has been investigated. When the coated alumina is thermally treated, the retention volumes of solutes increase on increasing the heating temperature from 200 to 600°C and then decrease with a further increase above 600°C. It is considered that this increase in retention volume is due to decomposition of the ammonium hexafluoroaluminate formed by reaction of the alumina with ammonium fluoride and concurrent formation of β-aluminum fluoride on the alumina surface. Optimal conditions for the preparation of the modified alumina with good characteristics for gas–solid chromatography involve selecting a post-heating temperature at which any conversion of ammonium hexafluoroaluminate into other compounds, especially β-aluminum fluoride, is prevented.

INTRODUCTION

Modifications of the surface properties of silica gel and alumina adsorbents for gas–solid chromatography (GSC) have been studied by coating with an inorganic salt, because salt-modified adsorbents have advantages such as high thermal stability (no bleeding from columns) and selective separations (*e.g.*, separation of *cis*- and *trans*-isomers).

In previous papers[1,2] it was reported that a salt-modified alumina adsorbent giving symmetrical peaks for C_5–C_8 hydrocarbons can be prepared by treatment with potassium fluoride–hydrofluoric acid solution or by coating with alkali metal fluorides. In these methods, it was found that a new surface layer, consisting of $M_xAlF_{3+x}(H_2O)_{3-x}$ and insoluble in water, was formed on the alumina surface by reaction with the alkali metal fluoride and the alumina. The adsorption activities and specific surface areas of these modified alumina adsorbents were varied through different extents of formation of $M_xAlF_{3+x}(H_2O)_{3-x}$ by post-heating treatment at various temperatures.

In this study, modification of activated alumina by coating with ammonium fluoride was studied as an extension of our previous studies with alkali metal fluorides.

EXPERIMENTAL

Reagents

Guaranteed reagent-grade ammonium fluoride was used as a modifier without further purification. Guaranteed reagent-grade or extra-pure reagent-grade aliphatic hydrocarbons with C_5–C_6 carbon atoms, benzene, toluene and ethylbenzene were used as organic solutes. Guaranteed reagent-grade p-nitrophenol and benzene, used for the determination of the specific surface area of the adsorbent, were purified by a single recrystallization and distillation, respectively.

Adsorbent

Activated alumina beads, Neobead MS.C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), were used for the preparation of modified alumina adsorbents. The alumina was coated with ammonium fluoride by evaporating 50 cm³ of a solution containing 20 g of the alumina and a required amount of ammonium fluoride on a water-bath. The salt-coated alumina was dried at 100°C for 2 h and, if necessary, post-heated at 200–1000°C before use.

Determination of ammonium and fluoride ions

The ammonium ion content of the modified alumina adsorbent was determined by the Kjeldahl method. Fluoride ion was determined by absorptiometry with Alfuson (Dojindo Labs., Kumamoto, Japan) as a colorimetric reagent after dissolution of the modified alumina in 1 M sodium hydroxide solution and removal of aluminium ion by extraction with 8-quinolinol into chloroform[3,4].

Determination of specific surface area

The specific surface area of the modified alumina was measured by adsorption of p-nitrophenol from benzene solution according to the method of Giles et al.[5].

Apparatus and gas chromatographic measurement

A Hitachi Model K-53 gas chromatograph equipped with a thermal conductivity detector and a stainless-steel column (100 × 0.3 cm I.D.) was used. Helium was used as the carrier gas at a flow-rate of 40 cm³ min⁻¹. A Hitachi Model QPD 33 recorder with a chart speed of 5 or 10 mm min⁻¹ and 1 mV full-scale was used to record the chromatograms. The column temperature was 180°C for aromatic hydrocarbons and 80°C for aliphatic hydrocarbons. A 0.2-μl dose of each solute was injected into the column with a 10-μl Termo MS-10 microsyringe. A Hitachi Model 101 spectrophotometer was used for measurement of the specific surface area and for the determination of fluoride ion.

RESULTS AND DISCUSSION

Effects of thermal treatment on activated alumina

Guillemin et al.[6] have reported that various aliphatic and aromatic hydrocarbons can be separated as symmetrical peaks by GSC on porous silica gels at 200°C. Thermal treatment of activated alumina was first examined in a wide temperature range of 200–1000°C.

Fig. 1 shows the gradual decrease in the specific retention volume, V_g, of benzene, toluene and ethylbenzene with increasing heating temperature. The thermal treatment of the activated alumina resulted in a reduced retention time for each solute but hardly improved the peak shape.

From a comparison of this result with that of Guillemin et al.[6], it appears that the alumina surface has more energetical heterogeneous adsorption than the silica gel surface. The thermal treatment decreases the adsorption activity and reduces the specific surface area of the alumina but slightly improves the energy for heterogeneous adsorption, which is regarded as an important cause of the appearance of tailed peaks. In order to prepare an adsorbent for GSC that give sharp and symmetrical peaks, it is necessary to convert the original alumina surface into a uniform and less adsorptive one such as the $M_xAlF_{3+x}(H_2O)_{3-x}$ layer obtained previously.

Ammonium fluoride is expected to act as a modifier capable of covering the original alumina surface with an ammonium hexafluoroaluminate layer by reaction and with another surface layer by thermal treatment.
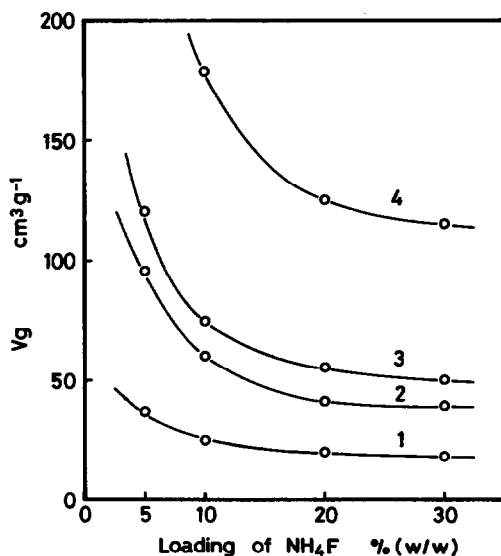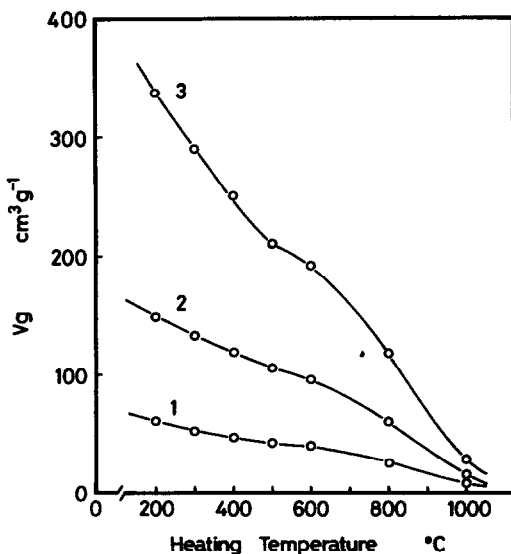

Fig. 1. Effect of thermal treatment of the unmodified alumina on the retention of aromatic hydrocarbons. Column temperature: 180°C. Solutes: 1, benzene; 2, toluene; 3, ethylbenzene.

Fig. 2. Effect of the amount of ammonium fluoride coated on the alumina on the retention of aliphatic hydrocarbons. Column temperature: 80°C. Solutes: 1, n-pentane; 2, cyclohexane; 3, n-hexane; 4, 1-hexene.

Modification of activated alumina with ammonium fluoride

The specific retention volumes of aliphatic hydrocarbons continuously decrease to constant values with an increase in the amount of ammonium fluoride coated (Fig. 2). This effect is also observed with aromatic hydrocarbons.

Fig. 3 shows a similar dependence of the specific surface area, σ_s, of the ammonium fluoride-coated alumina adsorbent on the amount of the salt. The graph of experimentally obtained specific retention volume of any solute against the specific surface area of the adsorbent measured by the *p*-nitrophenol method was linear with a large intercept on the abscissa, as shown in Fig. 4. This result indicates that the following relationship[7,8] holds:

$$V_g = K_s \sigma_s$$

where K_s is the distribution constant for adsorption.

Each straight line intersects the abscissa at the same point, so that this intercept can be regarded as the specific surface area of an apparently inert part for the solute retention. It is probable that part of the adsorbent surface can adsorb *p*-nitrophenol molecules from a benzene solution by hydrogen bonding but hydrocarbon solutes only with difficulty under·GSC conditions. From smoothly decreasing dependences of the specific retention volume and specific surface area on the amount of salt coated, it is reasonable to conclude that the highly adsorptive alumina surface has been successively covered with less adsorptive surface layers such as adsorbed ammonium fluoride, the ammonium hexafluoroaluminate formed and ammonium fluoride crystals.
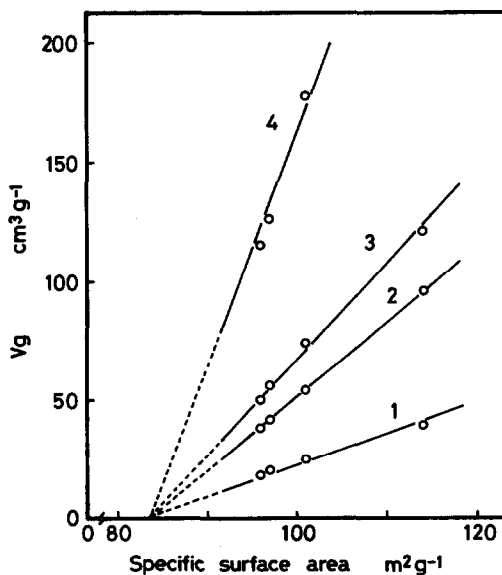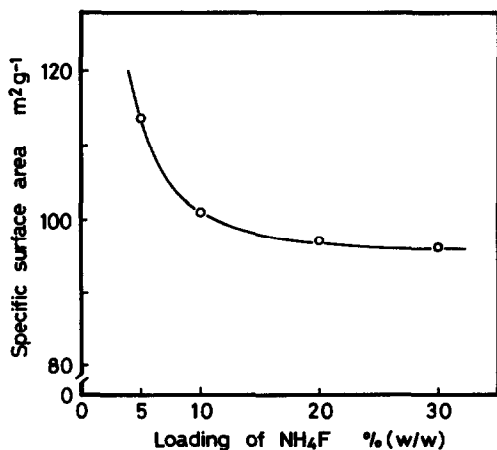

Fig. 3. Dependence of the specific surface area of the modified alumina on the salt loading.

Fig. 4. Variation of the retention of aliphatic hydrocarbons with the specific surface area of ammonium fluoride-coated alumina. Other details as in Fig. 2.

Post-heating treatment of alumina coated with ammonium fluoride

Fig. 5 shows the variation of the retention volume of some aromatic hydro-
carbons with the post-heating temperature using 10 and 30% (w/w) ammonium fluo-
ride-coated alumina adsorbents. In both instances the solute retention volume increa-
ses to a maximum at about 600°C with increasing post-heating temperature and then
decreased with a further increase above 600°C. Such a temperature dependence of
the solute retention volume is different from previous results obtained on alumina
modified with an alkali metal fluoride. This result suggests that different reactions
and crystallization of ammonium fluoride and its reaction products from those of
alkali metal fluorides occur during the post-heating treatment.

Fig. 6 shows the dependence of the retention volume of ethylbenzene on the
amount of ammonium fluoride coated at different post-heating temperatures. On the
ammonium fluoride-coated alumina post-heated above 600°C, a continuously de-
creasing trend, similar to the curve in Fig. 2, is observed. An increasing dependence
of the retention volume on the amount of the salt occurs on the ammonium fluo-
ride-coated alumina post-heated below 600°C. These results indicate that the post-
heating treatment of the ammonium fluoride-coated alumina below and above 600°C
causes activation and effective deactivation of the adsorbent surface, respectively, for
adsorption of hydrocarbon solutes under GSC conditions.

The specific surface area of the post-heated 10% (w/w) ammonium fluoride-
coated alumina simply decreases with increasing post-heating temperature (Fig. 7).
This result is similar to those obtained previously with modified alumina coated with
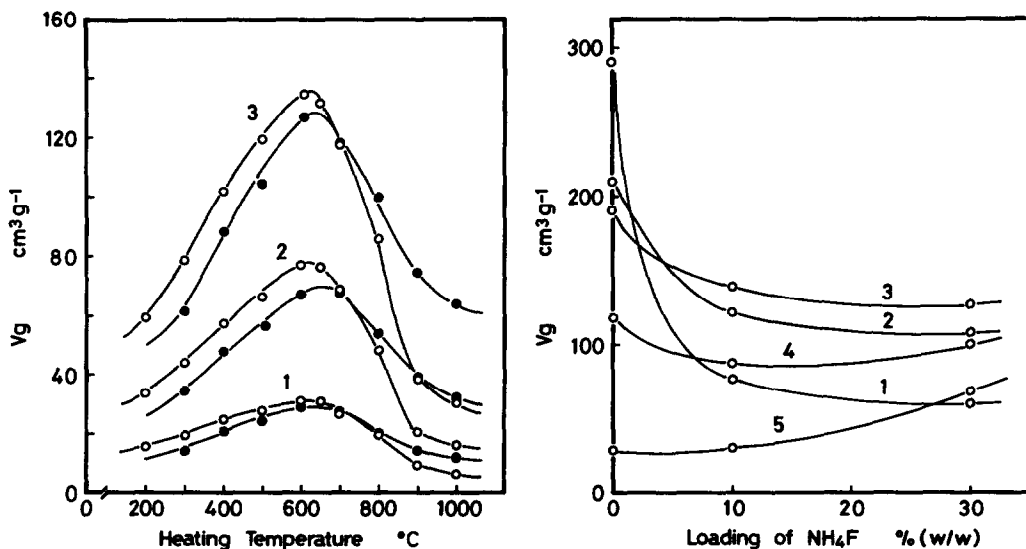an alkali metal fluoride but does not always correspond to the variation of the re-

Fig. 5. Effect of thermal treatment of the modified alumina on the retention of aromatic hydrocarbons.
Adsorbents: O, modified alumina coated with 10% ammonium fluoride; ●, modified alumina coated
with 30% ammonium fluoride. Other details as in Fig. 1.

Fig. 6. Variation of the retention of ethylbenzene with the salt loading. Column temperature: 180°C.
Post-heating temperature: 1, 300°C; 2, 500°C; 3, 600°C; 4, 800°C; 5, 1000°C.
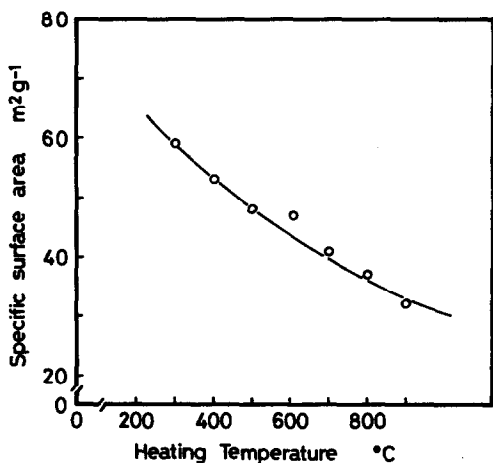
Fig. 7. Variation of the specific surface area of the modified alumina with post-heating temperature. Adsorbent: modified alumina coated with 10% ammonium fluoride.
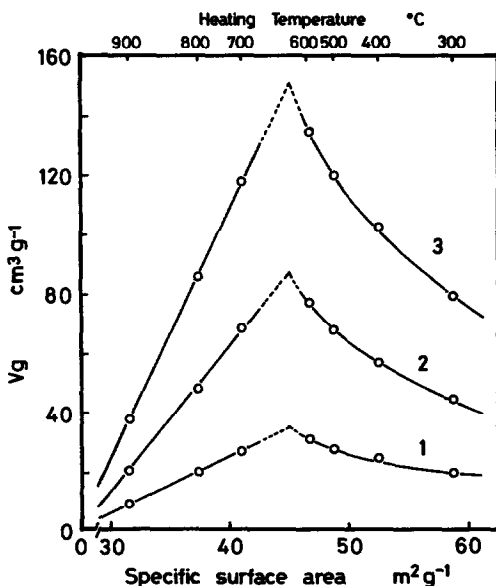
Fig. 8. Variation of the retention of aromatic hydrocarbons with the specific surface area of the post-heated modified alumina. Adsorbent as in Fig. 7. Other details as in Fig. 1.

tention volume of the solute. This result suggests that the retention volume depends on another factor besides the specific surface area. A graph of retention volume against specific surface area consists of a linearly increasing part and an exponentially decreasing part (Fig. 8). The linearly increasing part, representing the ammonium fluoride-coated alumina post-heated above 600°C, suggests that the alumina surface is completely covered with a surface layer with the same characteristics for adsorption of hydrocarbon solutes. The exponentially decreasing part, representing the retention volume *versus* specific surface area of the ammonium fluoride-coated alumina post-heated below 600°C, indicates that the adsorption properties of the adsorbent surface change gradually with successive decompositions and formation of ammonium fluoride and its reaction products such as ammonium hexafluoroaluminate on post-heating at increasing temperature.

In order to determine the true effect of the post-heating temperature of the ammonium fluoride-coated alumina, ammonium and fluoride ions in the adsorbent were determined. As shown in Fig. 9, the ammonium and fluoride ion contents of the 30% (w/w) ammonium fluoride-coated alumina decrease with increasing post-heating temperature. The ammonium ion content rapidly decreases to zero at temperatures up to 600°C. The fluoride ion content is reduced by post-heating treatments above 400°C. This result shows that the ammonium fluoride coated and its reaction products react and/or decompose on the alumina, first to lose ammonium ion and second to lose concurrently fluoride and ammonium ions with increasing post-heating temperature. Thus, the alumina surface may be covered with a different type of surface layer depending on the post-heating temperature.
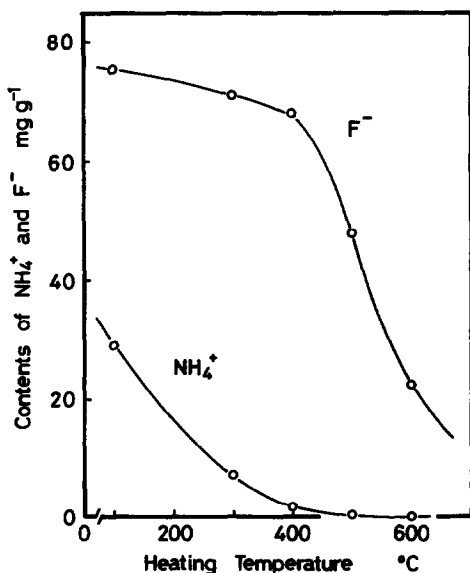
Fig. 9. Variation of the ammonium and fluoride ion contents in the modified alumina with post-heating temperature.

Moerkerken et al.[9] referred to the Netherlands patent[10] in which the reaction of ammonium fluoride with alumina proceeds in three stages, as shown in Fig. 10, and their results indicate that the loss of ammonium ion is completed by post-heating at 600°C. The large loss of fluoride ion by post-heating above 400°C is probably due to sublimation and/or decomposition of β-aluminum fluoride. From these results, it is concluded that the modification of surface properties of the ammonium fluoride-coated alumina is caused by the formation and decomposition of ammonium fluoride, ammonium hexafluoroaluminate and β-aluminum fluoride on post-heating. Also, the difference between the present and previous results is due to the different chemical behaviours of ammonium fluoride and alkali metal fluorides as the modifier.
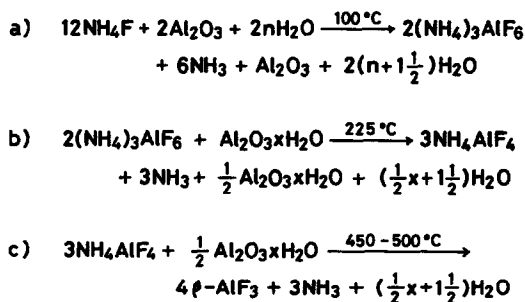
a) $12NH_4F + 2Al_2O_3 + 2nH_2O \xrightarrow{100\,°C} 2(NH_4)_3AlF_6$
$$+ 6NH_3 + Al_2O_3 + 2(n+1\tfrac{1}{2})H_2O$$

b) $2(NH_4)_3AlF_6 + Al_2O_3xH_2O \xrightarrow{225\,°C} 3NH_4AlF_4$
$$+ 3NH_3 + \tfrac{1}{2}Al_2O_3xH_2O + (\tfrac{1}{2}x+1\tfrac{1}{2})H_2O$$

c) $3NH_4AlF_4 + \tfrac{1}{2}Al_2O_3xH_2O \xrightarrow{450-500\,°C}$
$$4\beta-AlF_3 + 3NH_3 + (\tfrac{1}{2}x+1\tfrac{1}{2})H_2O$$

Fig. 10. Reaction of alumina with ammonium fluoride and with ammonium hexa- and tetrafluoroaluminate proposed for the manufacture of β-AlF$_3$ by the VKF process (Verenigde Kunstmest Fabrieken, Mekog-Albatros, Utrecht, The Netherlands).

When choosing suitable conditions for preparation of the ammonium fluoride-modified alumina adsorbent, it is important to select a post-heating temperature at which ammonium hexafluoroaluminate is stable on the alumina surface.

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