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

MODIFICATION OF ALUMINA WITH ALKALI METAL PHOSPHATES

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SUMMARY

Modified alumina adsorbents for gas-solid chromatography were prepared by coating activated alumina with trialkali metal phosphate and by heat treatment before and after coating. Their surface properties can be modified by controlling their preparation conditions. The modification of the surface properties can be understood on the basis of different dispersions of the trialkali metal phosphate on the alumina surface depending on the salt loading. It appears that the column performance is related to the homogeneity of the surface properties rather than the magnitude of the surface activity of the adsorbent with respect to adsorption. Gas-solid chromatographic columns packed with these adsorbents were characterized by good resolution for geometric isomers of aromatic hydrocarbons and their halogenated derivatives.

INTRODUCTION

The utility of gas-solid chromatography (GSC) expanded with the introduction of gas chromatography-mass spectrometry, gas-liquid-solid chromatography and micropacked columns. Modification of the surface properties of adsorbents for GSC, in order to remove restrictions to the analytical application of GSC, has been often studied by coating the active surface of the adsorbent with an inorganic salt^{1,2}. We have reported that some aliphatic and aromatic hydrocarbons and their halogeno derivatives with 5–8 carbon atoms can be well separated by GSC on modified alumina adsorbents prepared with the following modifying reagents: potassium fluoride-hydrofluoric acid solution³, alkali metal phosphate solution⁴, alkali metal fluorides⁵ and alkali metal chlorides⁶. The adsorption capacities of these modified alumina

adsorbents have been found to be dependent on the nature of the inorganic salt as a modifier, the salt loading and the temperatures of the pre-heating and post-heating treatments.

This paper describes the effects of such preparation conditions on the performance of columns packed with modified alumina adsorbents and on their adsorption capacities as an extension of the procedure for treating the alumina with alkali metal phosphate solution.

EXPERIMENTAL

Reagents

The organic solutes and inorganic salts were either guaranteed reagent-grade or extra-pure reagent-grade commercial materials, and were used without further purifications except for *p*-nitrophenol (an adsorbate) and benzene (solvent for measurement of the specific surface area of adsorbents), which were purified by recrystallization and distillation, respectively.

Aqueous solutions containing equimolar amounts of either crystalline disodium hydrogen phosphate and sodium hydroxide or dipotassium hydrogen phosphate anhydride and potassium hydroxide were used as trisodium phosphate and tripotassium phosphate solutions, respectively. A mixture of caesium carbonate and concentrated phosphoric acid in a molar ratio of Cs to PO_4^{3-} of 3:1 was applied as tricaesium phosphate solution. A suspension of trilithium phosphate precipitate was used because of the low solubility of this salt in water.

Adsorbents

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 pre-heated at 180–1100°C for 2 h before coating with alkali metal phosphate. The alumina pre-heated at a temperature higher than 1000°C was resieved to obtain a 60–80-mesh fraction. The alumina was coated with trisodium, tripotassium and tricaesium phosphates by evaporating about 30 ml of solution containing 15 g of the alumina and the required amount of each phosphate on a water-bath. Because of the low solubility of trilithium phosphate in water, coating was effected as follows. To 30 ml of a suspension of the required amount of this salt, 15 g of alumina were added and the mixture was allowed to stand with occasional stirring until the trilithium phosphate precipitate disappeared. The suspension was then evaporated to dryness on a water-bath.

All of the alumina samples coated with trialkali metal phosphates were dried at 180°C for 3 h and post-heated at 500–1000°C for 2 h. The modified alumina adsorbent was packed into a stainless-steel column after resieving.

Chromatography

A Hitachi K-23 gas chromatograph equipped with a thermal conductivity detector and a stainless-steel column (100 × 0.3 cm I.D.) was used in conjunction with a Hitachi QPD 33 recorder for gas chromatography. Helium was used as the carrier gas at a flow-rate of 40 ml/min. A 0.2- μl dose of each organic solute was injected into the column with a Terumo MST-10 microsyringe.

The procedures described previously⁵ were applied for measurement of the retention volume of the solute and its corrections, and for determination of the specific surface area of the modified alumina adsorbents.

RESULTS AND DISCUSSION

In other work^{5,6}, the adsorption capacities of the modified alumina adsorbents were found to be significantly influenced by thermal treatment both before and after coating with alkali metal fluoride or chloride. We first examined the effects of both pre- and post-heating treatments on the retention volume of a solute on the column packed with the modified alumina adsorbent coated with tripotassium phosphate at a salt loading of 0.24 mmole/g of free alumina.

Fig. 1 shows that the specific retention volume, V_g , of *n*-hexane remains almost constant irrespective of the post-heating temperature when the modified alumina adsorbent was post-heated at a temperature lower than its pre-heating temperature,

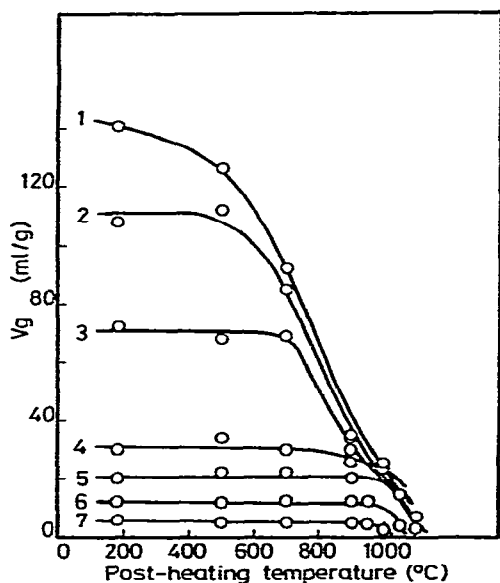


Fig. 1. Effect of thermal treatment of the alumina on the retention of *n*-hexane on alumina with coated tripotassium phosphate (0.24 mmol/g of free alumina). Column temperature: 80°C. Pre-heating temperature of the alumina: 1, without pre-heating; 2, 500; 3, 700; 4, 900; 5, 1000; 6, 1050; 7, 1100°C.

but decreases with increasing post-heating temperature on an adsorbent post-heated at a higher temperature. A large decrease in the specific retention volume is observed with increase in post-heating temperature on an adsorbent pre-heated at a lower temperature. Thus, the effect of the pre-heating treatment controls the adsorption capacities of the modified alumina adsorbents even if they are post-heated below the pre-heating temperature, whereas the post-heating treatment influence the adsorption capacities when the modified alumina adsorbents are post-heated above the pre-heating temperature. A decrease in the specific retention volume in this instance is

considered to be due mainly to sintering of the alumina particles as a result of by thermal treatment.

On the modified alumina adsorbents coated with different trialkali metal phosphates, the specific retention volumes of *n*-hexane and 1-hexene increased with trialkali metal phosphate coatings in the order $\text{Na}_3\text{PO}_4 < \text{Li}_3\text{PO}_4 < \text{K}_3\text{PO}_4 < \text{Cs}_3\text{PO}_4$, regardless of the pre-heating temperature. Also, their specific surface areas, σ_s , showed a similar regularity. $\text{Li}_3\text{PO}_4 < \text{Na}_3\text{PO}_4 < \text{K}_3\text{PO}_4 < \text{Cs}_3\text{PO}_4$. Further, the adsorption constants, K_s , of *n*-hexane and 1-hexene on these adsorbents, calculated from the equation $V_g = K_s\sigma_s$, increased with phosphate coatings in the order $\text{Na}_3\text{PO}_4 < \text{K}_3\text{PO}_4 < \text{Cs}_3\text{PO}_4 < \text{Li}_3\text{PO}_4$ and $\text{Cs}_3\text{PO}_4 < \text{K}_3\text{PO}_4 < \text{Na}_3\text{PO}_4 < \text{Li}_3\text{PO}_4$, respectively. These regularities suggest that the alkali metal ions dispersed on the adsorbent surface may act as active sites for adsorption of hydrocarbon solutes on the modified alumina adsorbents.

Depending on the nature of the trialkali metal phosphate, the specific retention volume of the solute showed a different variation with increase in the post-heating temperature, although the specific surface area of the adsorbent decreased continuously. Such a difference is considered to be caused as described previously⁵, by different courses of surface reactions and/or regular recrystallization of the phosphate coating or its reaction products because of their different melting points.

In Fig. 2, the specific retention volumes of *n*-hexane and 1-hexene on modified alumina adsorbents coated with trisodium or trilithium phosphate decrease monotonously with increase in the salt loading and, on adsorbents coated with tripotassium phosphate, pass through minima and maxima near salt loadings of 0.24 and

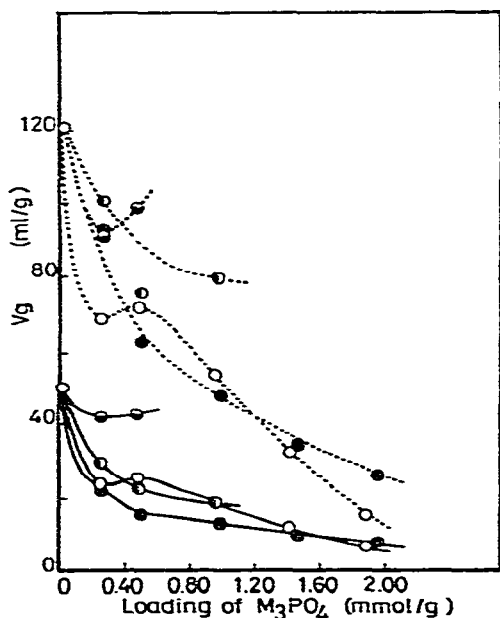


Fig. 2. Effect of the amount of salt coated on the alumina on the retention of *n*-hexane (—) and 1-hexene (---). Column temperature: 80°C. Pre-heating temperature of the alumina: 900°C. Post-heating temperature of the modified alumina: 900°C. Salt coated: ○, Li_3PO_4 ; ●, Na_3PO_4 ; ○, K_3PO_4 ; ●, Cs_3PO_4 .

0.48 mmole/g of free alumina. Those on the adsorbents coated with tricaesium phosphate showed minima near a salt loading of 0.24 mmole/g of free alumina.

Fig. 3 shows that the specific surface areas of these adsorbents, except for those coated with trilithium phosphate, increased smoothly with increasing salt loading.

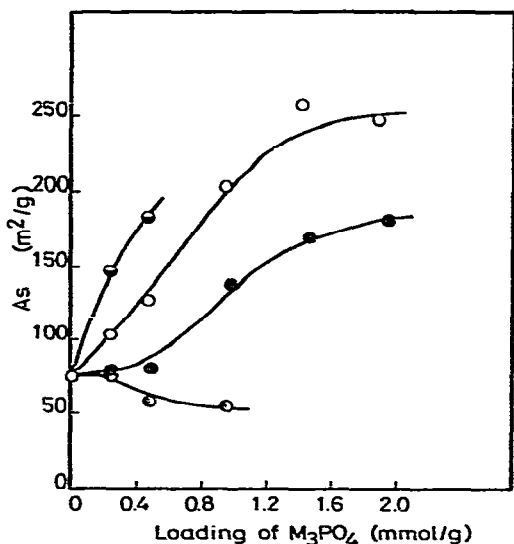


Fig. 3. Variation of specific surface area of the modified alumina adsorbents with the amount of salt coated on the alumina. Adsorbents as in Fig. 2.

Such differences between the trends in the variation of specific retention volume and specific surface area indicate that the specific surface area measured by the *p*-nitrophenol method⁷ differs from that utilized for solute retention in the GSC system. It is probable that, on the surface of the trialkali metal phosphate layer, *p*-nitrophenol molecules can be strongly adsorbed by hydrogen bonding but the hydrocarbon solute molecules can be weakly adsorbed in the GSC system. The results in Figs. 2 and 3 can be understood by considering that the alumina surface is progressively covered with a trialkali metal phosphate layer on increasing the salt loading. This concept is supported by the gradual decrease in the adsorption constant of the solute with increase in the salt loading (Fig. 4).

In this instance, the adsorption constants of *n*-hexane and 1-hexene also increased with the nature of the alkali metal ion of the phosphate coated in the same orders as observed previously. These regularities almost correlate with those of the ionic size of the alkali metal ions or their ionic charge densities. The solute retention in the GSC system can thus be expected to be dependent on intermolecular interactions between the solute molecule and the alkali metal ion as an active site for adsorption.

According to Kiselev's concept⁸, the ratio of the specific retention volume of *n*-hexane to that of *n*-pentane, $V_{g_{n\text{-hexane}}}/V_{g_{n\text{-pentane}}}$, can be thought of as a measure of the magnitude of non-specific interactions and the ratio of the specific retention volume of 1-hexene to that of *n*-hexane, $V_{g_{1\text{-hexene}}}/V_{g_{n\text{-hexane}}}$, as a measure of the

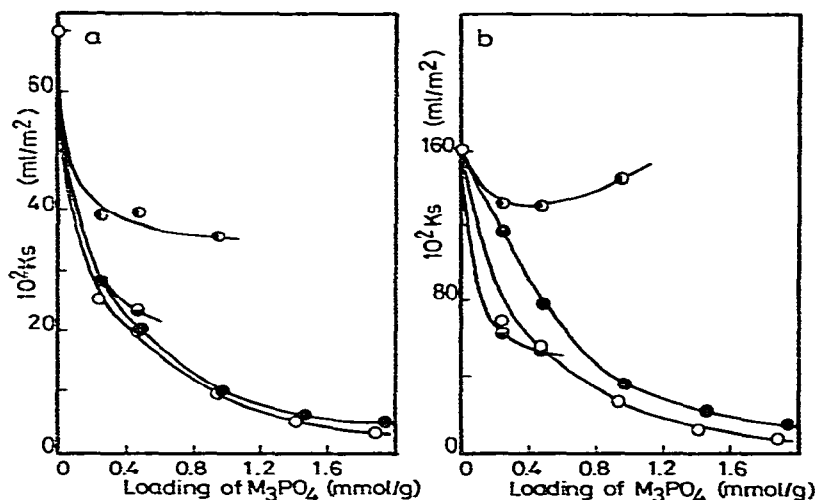


Fig. 4. Variation of adsorption constants of (a) *n*-hexane and (b) 1-hexene at 80°C on the modified aluminas with the amount of salt coated. Adsorbents as in Fig. 2.

strenght of the specific interactions between the adsorbate molecules and the adsorbent surface.

Fig. 5 shows that the ratio $V'_{g\text{-hexane}}/V'_{g\text{-pentane}}$ suddenly and then gradually decreased to a fixed value with increase in the salt loading, and that the ratio $V'_{g\text{-hexane}}/V'_{g\text{-hexane}}$ passed through a maximum near a salt loading of 0.24 mmole/g of free alumina and subsequently reached a constant value. These results suggest that the nature of the active site for adsorption is changed by coating with trialkali metal phosphate. A sudden decrease in the ratio $V'_{g\text{-hexane}}/V'_{g\text{-pentane}}$ and a rapid increase in the ratio $V'_{g\text{-hexane}}/V'_{g\text{-hexane}}$ were considered to be due to a decrease in the size of

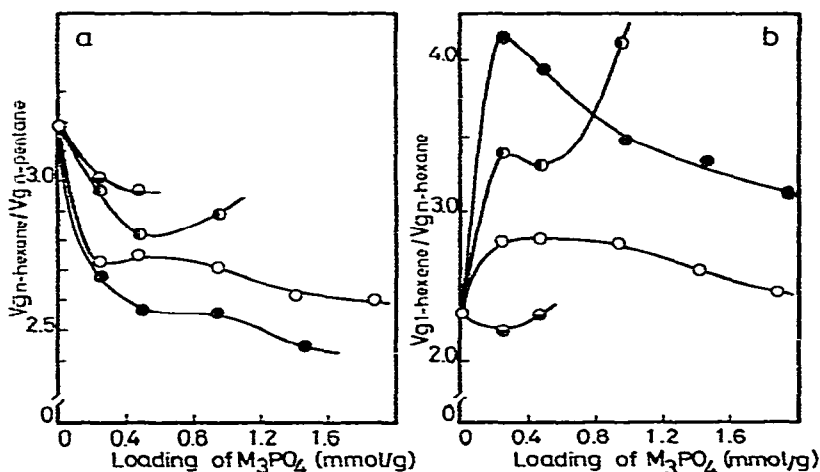


Fig. 5. Variation of relative retention with amount of salt coated. Column temperature: 80°C. Adsorbents as in Fig. 2.

the active site for adsorption. It is probable that hydroxyl groups and positively charged regions of the alumina surface act as active sites and are converted into alkali metal ion sites by selective shielding with trialkali metal phosphate. This is the case for monomolecular dispersion of alkali metal phosphate on the alumina surface. Such an alumina surface was simply considered to be deactivated and made homogeneous in energetical by successive blocking of the original active sites with trialkali metal phosphate dispersed as ions and/or ion pairs. After complete shielding of the original active sites, an excess of the trialkali metal phosphate may further cover, probably as an expanding layer, the alumina surface deactivated by monomolecular dispersion of the salt. It is likely that a gradual decrease in both $V_{g_{m\text{-hexane}}}/V_{g_{m\text{-pentane}}}$ and $V_{g_{1\text{-hexene}}}/V_{g_{m\text{-hexane}}}$ is due to such progressive shielding with the trialkali metal phosphate layer.

Fig. 6 indicates that the relative peak sharpness⁹ for *m*-chlorotoluene, *m*-dichlorobenzene and 1,2,4-trimethylbenzene showed maxima near salt loadings of 0.24–0.96 mmole/g of free alumina. These curves are similar to the $V_{g_{1\text{-hexene}}}/V_{g_{m\text{-hexane}}}$ versus salt loading curves in Fig. 5. However, the relative peak sharpness did not show an apparent regularity with the nature of the phosphate coating. With increasing salt loading, the width of each peak was observed to decrease to a minimum with an improvement in peak shape from asymmetric to symmetrical and an increase through the minimum. This observation suggests that the surface properties of the modified alumina adsorbent were homogeneous by selective shielding of the original active site

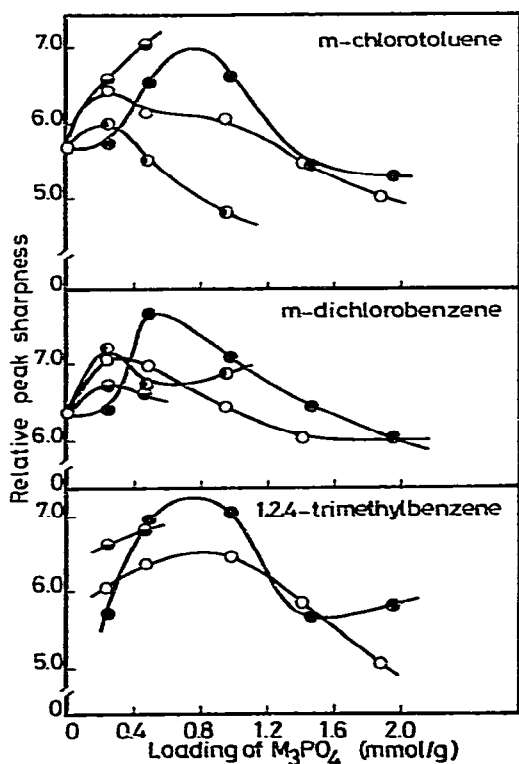


Fig. 6. Variation of relative peak sharpness of eluted peak with amount of salt coated. Column temperature: 180°C. Adsorbents as in Fig. 2.

with the trialkali metal phosphate. From these results, the column performance may be related to the homogeneity of the surface properties rather than the magnitude of the adsorption capacities of the modified alumina adsorbent packed into the column. Hence the results obtained can be understood by considering the different dispersions of the trialkali metal phosphate on the alumina surface depending on the salt loading.

The modified alumina adsorbents are characterized by good resolution for geometric isomers of aromatic compounds such as chlorotoluene and dichlorobenzene. It should be noted that the separation of the peaks of *m*-xylene and *p*-xylene could be partly achieved, as shown in Fig. 7, on only a 2-m column packed with the modified alumina adsorbent coated with tripotassium phosphate, but not on the columns packed with the adsorbent coated with the other trialkali metal phosphates.

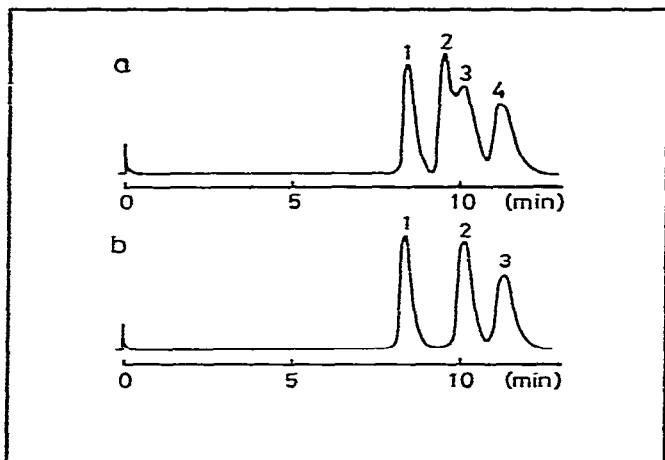


Fig. 7. Chromatograms of mixtures of (a) xylene isomers and (b) chlorotoluene isomers. Column temperature: (a) 150°C; (b) 160°C. Column length: 2 m. Column packing: alumina coated with tripotassium phosphate (0.24 mmol/g of free alumina) with pre-heating at 1100°C and post-heating at 950°C. Peaks: (a) 1 = ethylbenzene; 2 = *m*-xylene; 3 = *p*-xylene; 4 = *o*-xylene; (b) 1 = *o*-chlorotoluene; 2 = *m*-chlorotoluene; 3 = *p*-chlorotoluene.

Such differences in resolution depending on the nature of the trialkali metal phosphate can be interpreted only with difficulty on the basis of the above discussion. A complete understanding may require more detailed information of the surface structure of the modified alumina adsorbent. An alternative investigation of the quantitative interpretation of solute retention in GSC is now in progress.

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