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

### MODIFICATION OF ALUMINA WITH ALKALI METAL CHLORIDE

AKIO FUKAZAWA\*, SADA AKI MORIGUCHI, KUNISHIGE NAITO\* and SHINSUKE TAKEI

*Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Hitachi (Japan)*

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#### SUMMARY

Variations in the surface properties of salt-modified alumina adsorbents have been studied by coating alumina with alkali metal chlorides and by heating before and after coating. The changes found were not based on simple blocking of active sites for adsorption with the salt coated, but on continuous shielding with a new surface layer formed by reaction of the alumina with the salt through the post-heating treatment. Sodium chloride modified alumina showed good peak resolution for gas-solid chromatographic separation of geometric isomers of 2-olefins and polychloro derivatives of benzene. This adsorbent gave a sharp and symmetrical peak for all solutes investigated.

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#### INTRODUCTION

In order to obtain adsorbents with desirable and interesting characteristics for gas-solid chromatography (GSC), the coating of highly adsorptive adsorbents with various inorganic salts has been studied<sup>1-6</sup>. In those investigations, attention was focused chiefly on the influence of the nature of the salt on the solute retention data measured on adsorbents coated with fixed amounts of the salt, rarely on the effect of the salt loading and heat treatments either before or after coating.

We have reported that very effective modification is achieved by forming a new surface layer of potassium fluoroaluminate through treatment of alumina with a HF-KF mixed solution or by coating with potassium fluoride<sup>7,8</sup>. It has been pointed out that heat treatment significantly influences the adsorption capacity of salt-modified alumina coated with alkali metal phosphate and with dipotassium hydrogenphosphate<sup>9,10</sup>.

In this paper, the modification of the surface properties of alumina with alkali

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\* Present address: Nissan Chemical Industry, Co. Ltd., Central Research Laboratory, Funabashi, Japan.

metal chloride is described mainly from the viewpoint of the effect of heat treatment and the dependence on a salt loading.

## EXPERIMENTAL

Extra pure reagent grade lithium, sodium and potassium chlorides were used without further purification. Caesium chloride was prepared from extra pure reagent grade caesium carbonate dihydrate and a small excess of concentrated hydrochloric acid, and purified by removal of excess of hydrochloric acid by evaporation. The organic solutes used were commercial materials of guaranteed reagent grade or extra pure reagent grade. *p*-Nitrophenol and benzene used for measurement of the specific surface areas of the adsorbents were purified by previous methods<sup>9</sup>.

Activated alumina beads, Neobead MS C (60–80 mesh) (Mizusawa Industrial Chemicals, Tokyo, Japan), were first pre-heated for 2 h at a temperature of 200–1100°C before coating. The coating of alumina with alkali metal chloride was performed by evaporation of 30 ml of a solution containing 15 g of the pre-heated alumina and a known amount of the salt on a water-bath with an occasional stirring. After coating, the salt-coated alumina was dried for 3 h at 120°C and then post-heated at a temperature between 500 and 1100°C for 2 h. The salt-modified alumina adsorbent thus prepared was packed into a stainless-steel column (100 × 0.3 cm I.D.). This column was pre-conditioned for 3 h at 180°C in a helium gas stream at a flow-rate higher than 40 ml/min before use.

A Hitachi 063 gas chromatograph equipped with a thermal conductivity detector and a Hitachi 056 recorder was used. The gas chromatographic (GC) conditions applied were as described previously<sup>8</sup>. The measurement of solute retention volumes and their corrections, and the determination of the specific surface areas of the adsorbents, were carried out as described previously<sup>8</sup>.

## RESULTS AND DISCUSSION

On the salt-free alumina without post-heating treatment, the retention volume of all the solutes investigated decreased gradually with increasing pre-heating temperature up to 700°C and greatly with a further increase above this. On the post-heated alumina a reduced and almost constant retention volume was observed independent of the pre-heating temperature when below the post-heating temperature. With increasing the pre-heating temperature above the latter, a sudden decrease in the retention volume was observed but this decrease became smaller with increasing post-heating temperature. These results, coincident with previous ones<sup>10</sup>, suggest that the adsorption capacity of the salt-free alumina can easily be controlled by adjusting the pre-heating and/or the post-heating temperature.

Fig. 1 shows the salt loading dependence of the specific retention volume,  $V_g$ , of benzene on NaCl-coated alumina pre-heated at 300, 500 and 900°C and only dried at 200°C after coating. Independent of the pre-heating temperature, the specific retention volume of benzene decreased simply to zero with increasing salt loading. In another experiment, no adsorptive interaction was found between benzene molecules and the surface of sodium chloride crystals at 180°C. These results suggest that the active sites for adsorption on the alumina surface are successively blocked by coating

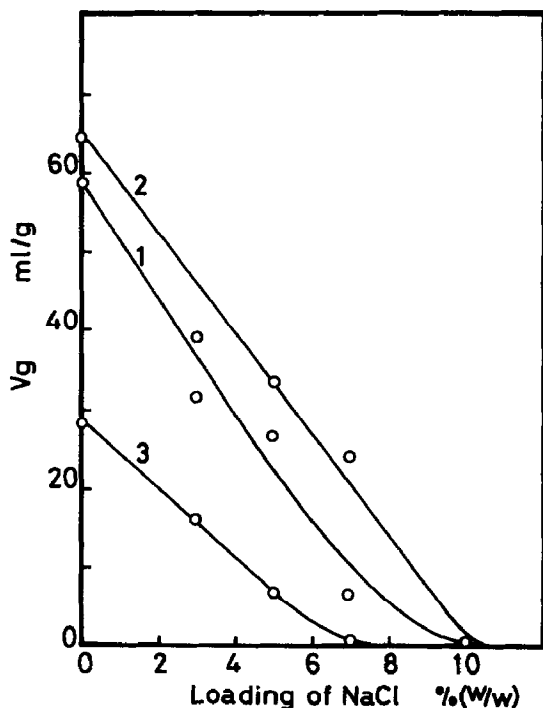


Fig. 1. Salt loading dependence of the specific retention volume of benzene on NaCl-coated alumina without post-heating treatment. Pre-heating temperatures: 1, 300°C; 2, 500°C; 3, 900°C.

with an increasing amount of sodium chloride and finally the alumina surface is completely covered with sodium chloride crystals. It should be noted that even a highly adsorptive alumina surface can be completely shielded with sodium chloride crystals at *ca.* 10% (w/w) salt loading. By selecting the salt loading, the adsorption capacity of the alumina adsorbent can be properly controlled, but these NaCl-coated adsorbents are not practically useful because of the appearance of tailed peaks on the chromatograms. In order to obtain adsorbents which yield sharp and symmetrical peaks, post-heating of the salt-coated alumina is necessary.

Fig. 2 shows the salt loading dependence of the specific retention volume of benzene on NaCl-coated alumina pre-heated at 300, 500, 700, 900 and 1100°C and post-heated at 700°C, which is somewhat different from that shown in Fig. 1. With increasing salt loading, the specific retention volume gradually decreased to a fixed value depending upon the pre-heating temperature. This suggests that the more adsorptive alumina surface is successively covered with a less adsorptive surface layer. The latter is different from sodium chloride crystals because the specific retention volume is not zero even at 20% (w/w) salt loading. From the large decrease in chloride content of the adsorbent upon post-heating treatment, it is reasonable to conclude that a sodium aluminate layer, which is less adsorptive, is formed by reaction of alumina with sodium chloride in the presence of adsorbed water, although we failed to confirm this by means of X-ray diffraction.

At any salt loading, the specific retention volume increased with increasing pre-heating temperature from 300 to 500°C and then decreased with a further increase

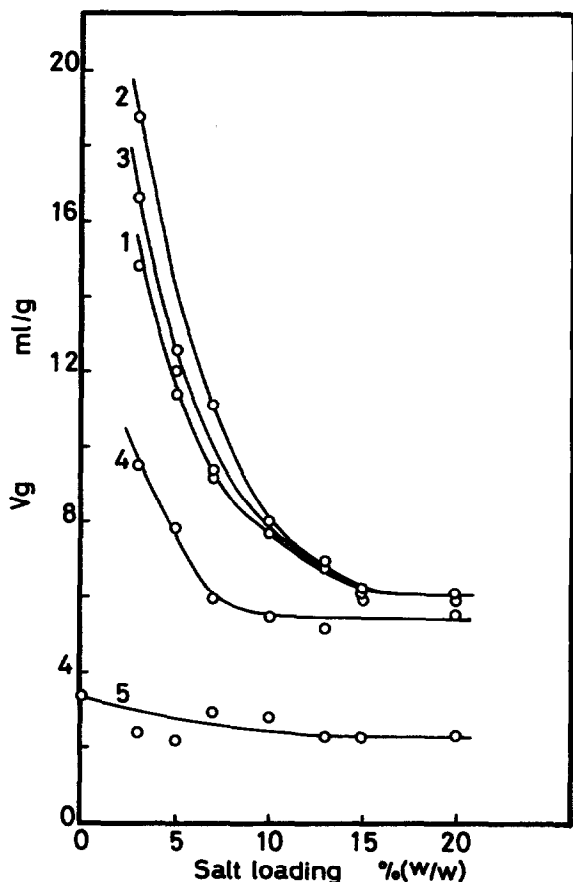


Fig. 2. Salt loading dependence of the specific retention volume of benzene on NaCl-coated alumina post-heated at 700°C. Pre-heating temperatures: 1, 300°C; 2, 500°C; 3, 700°C; 4, 900°C; 5, 1100°C.

in the pre-heating temperature. This trend is very similar to that of alumina itself. From experimental data obtained on the 10% (w/w) NaCl-coated alumina pre-heated at 500 and 900°C and post-heated at 900°C, the distribution constant for adsorption,  $K_s$ , for a given solute can be calculated according to the relationship

$$K_s = V_g/\sigma_s$$

where  $\sigma_s$  is specific surface area of the adsorbent (Table I) and found to be the same at each pre-heating temperature. This suggests that the less adsorptive surface layer is distributed in the same form on the alumina regardless of the pre-heating temperature. Thus, the post-heating treatment of the salt-coated alumina results in the formation of a uniform and less adsorptive surface layer on the alumina, and a significant improvement in peak shape for any solute. The NaCl-coated alumina was characterized by good resolution in GSC separation of geometric isomers of 2-olefins and of polychloro-substituted derivatives of benzene. A high pre-heating temperature (1100°C) and a high salt loading (20%, w/w) gave less good resolution.

TABLE I

DISTRIBUTION CONSTANTS FOR ADSORPTION ( $10^{-5}$  cm) ON THE 10% (w/w) NaCl-COATED ALUMINA ADSORBENT

Solute	Pre-heating temperature	
	500°C	900°C
Benzene	0.8	0.9
Toluene	1.7	1.8
Ethylbenzene	3.0	3.1
<i>p</i> -Xylene	3.2	3.4
<i>m</i> -Xylene	3.4	3.6
<i>o</i> -Xylene	3.8	4.0
<i>n</i> -Pentane	1.0	1.1
<i>n</i> -Hexane	2.7	2.8
Cyclohexane	1.9	2.1
<i>trans</i> -2-Butene	1.3	1.3
<i>cis</i> -2-Butene	1.5	1.6

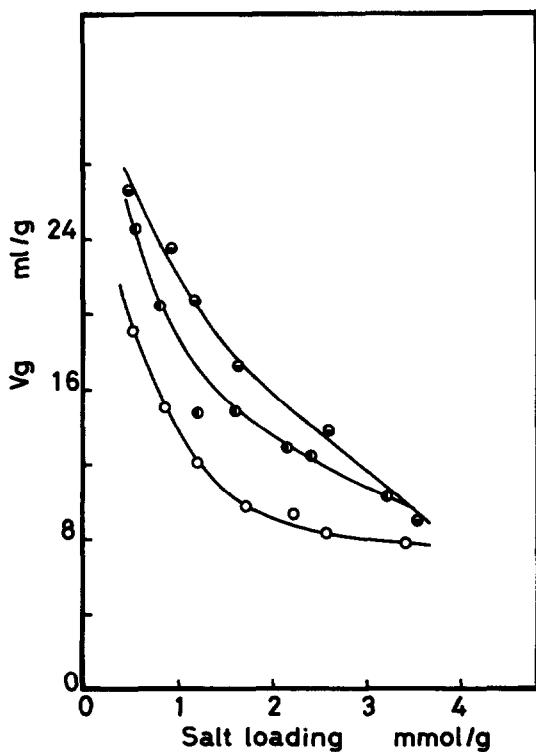


Fig. 3. Salt loading dependence of the specific retention volume of toluene on salt-coated alumina pre-heated and post-heated at 900°C. Salt coated: ●, LiCl; ○, NaCl; ●, KCl.

In Fig. 3 a gradual decrease in the specific retention volume of toluene with increasing salt loading is seen on LiCl-, KCl- and NaCl-coated alumina adsorbents heated at 900°C before and after coating. At any salt loading, the specific retention volume increased with the nature of the salt coated in the order, NaCl < KCl < LiCl. On the other hand, Fig. 4 shows that the specific surface area of the KCl- and NaCl-

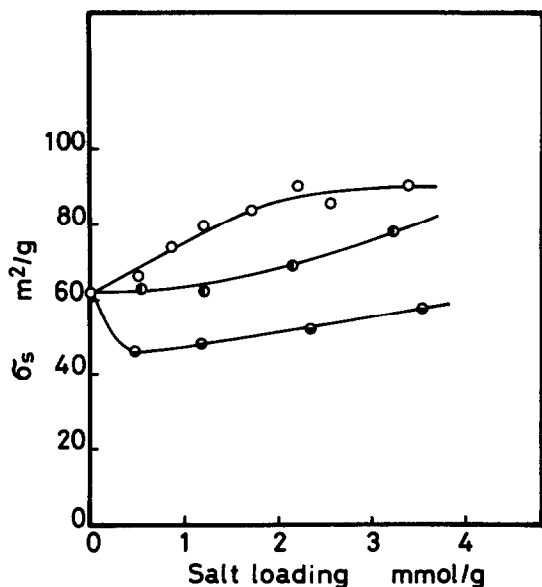


Fig. 4. Salt loading dependence of the specific surface area of salt-coated alumina pre-heated and post-heated at 900°C. Key as in Fig. 3.

coated alumina adsorbents increased smoothly, but that of the LiCl-coated alumina first decreased and then increased with increasing salt loading. The specific surface area also increased with the nature of the salt in the order, LiCl < KCl < NaCl. These trends are the reverse of those of the specific retention volume. It is probable that hydrocarbon molecules are adsorbed by a positively charged entity such as an alkali metal ion or an aluminium ion coordinated incompletely with oxide and/or hydroxide anions under the GSC conditions. *p*-Nitrophenol molecules can interact further with another part of the adsorbent surface through hydrogen bonding. It appears that the above difference is caused by a difference in the type and the strength of adsorptive interactions between *p*-nitrophenol or hydrocarbon molecules and the active sites for adsorption on the alumina surface. This suggests that the whole of the specific surface area measured by the *p*-nitrophenol method<sup>11</sup> is not always available for the solute retention in GSC. Thus, an alkali metal aluminate layer can be considered as a surface layer with such adsorption properties. A gradual decrease in the specific retention volume and a smooth increase in specific surface area can be understood in terms of the successive coverage of the adsorbents with the alkali metal aluminate layer with increasing salt loading. The distribution constant for adsorption of any solute first increased and then gradually decreased on the LiCl- and KCl-coated alumina adsorbents, and only decreased on the NaCl-coated alumina, with increasing salt load-

ing. The decreasing trend indicates that the alkali metal aluminate layer shows a less adsorptive interaction towards hydrocarbon solutes than the original alumina surface. The dependence of the distribution constant for adsorption on the nature of the salt coated is not always coincident with the order in the alkali metal ion size, in contrast to previous observations<sup>7,8</sup>. This is caused by the fact that the salt coated is not present in the regularly crystalline form or in the same circumstance for the alkali metal ion, that is, the alkali metal aluminate layer formed is almost amorphous. (It shows no characteristic peak on the X-ray diffraction pattern.) Therefore, it is not reasonable to discuss the retention data in terms of the non-specific and specific interactions between the solute molecules and the alkali metal ions as active sites for adsorption.

In Fig. 5 the specific retention volume of ethylbenzene decreases with increasing pre-heating temperature similarly on the salt-coated (1.9 mmol/g) and the salt-free alumina adsorbents post-heated at 900°C. The specific retention volume decreased with the nature of the salt in the order, none > CsCl > LiCl > KCl > NaCl, at any other temperature than 700°C. The specific surface area of the salt-coated alumina adsorbent decreased with increasing pre-heating temperature above 500°C, while that of the salt-free alumina was maximal at 700°C. A change in the specific retention volume can reasonably be compared with that of the specific surface area of the adsorbent with pre-heating temperature. The distribution constant for ad-

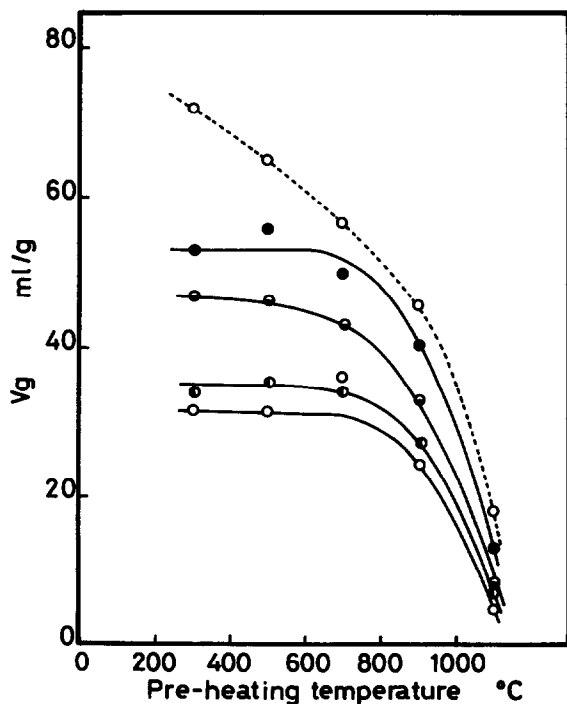


Fig. 5. Dependence of the specific retention volume of ethylbenzene upon pre-heating temperature on 1.9 mmol/g salt-coated alumina post-heated at 900°C. Salt coated:  $\ominus$ , LiCl;  $\circ$ , NaCl;  $\bullet$ , KCl;  $\bullet$ , CsCl.  $\circ$ --- $\circ$ , Salt-free alumina.

sorption is almost constant on the salt-coated alumina adsorbent pre-heated at a temperature below the post-heating temperature. Under these conditions, the specific retention volume is dependent on the specific surface area of each salt-coated alumina adsorbent. By post-heating the salt-coated alumina at a fixed temperature above the pre-heating one, a surface layer with the same adsorptive interactions towards hydrocarbon solutes can be realized but the specific surface area is dependent on the pre-heating temperature. In this case, it is reasonable to consider that the alumina surface is completely covered with the alkali metal aluminate layer. The large decrease in the specific retention volume with increasing pre-heating temperature above 900°C is due mainly to the decrease in specific surface area caused by the pre-heating treatment and to a slight decrease in the distribution constant for adsorption. From X-ray diffraction experiments it was found that the large decrease in the specific surface area in this temperature range is due to a phase transition of the bulk alumina. The slightly reduced distribution constant for adsorption is due probably to a change in the distribution of the surface layer formed on the alumina because a large decrease in specific surface area yields a sudden increase in the amount of salt per unit surface area. The dependence of the specific retention volume on the pre-heating temperature can be regarded as that on the salt loading in mol/m<sup>2</sup>.

Fig. 6 shows the dependence of the specific retention volume of ethylbenzene upon the post-heating temperature from 500 to 1100°C on 1.9 mmol/g salt-coated

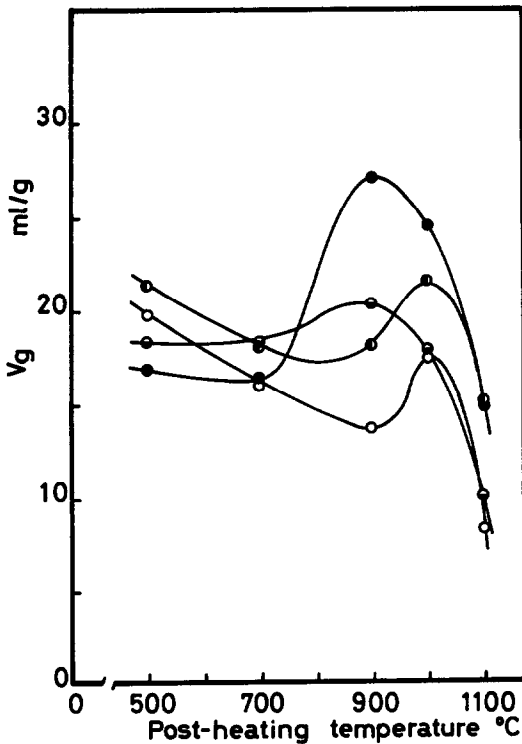


Fig. 6. Dependence of the specific retention volume of ethylbenzene upon post-heating temperature on 1.9 mmol/g salt-coated alumina pre-heated at 1000°C. Salt coated: ○, LiCl; ◻, NaCl; ◊, KCl; ●, CsCl.



alumina pre-heated at a fixed temperature of 1000°C. The maximum value of the specific retention volume occurs at the post-heating temperature of 900°C on the LiCl- and CsCl-coated alumina adsorbents and the minimum and maximum values at 900 and 1000°C respectively on the NaCl- and KCl-coated ones.

The LiCl-, KCl- and CsCl-coated alumina adsorbents have maximum specific surface areas at 900°C, but the NaCl-coated alumina at 700°C. The change in the specific retention volume on the LiCl-coated alumina is similar to that of the specific surface area with post-heating temperature. Such a good correspondence between the specific retention volume and the specific surface area is not observed on the other salt-coated alumina adsorbents. These results suggest that the different post-heating treatments yield surface layers with different adsorptive interactions towards hydrocarbon solutes. Such different adsorptive properties are caused probably by different extents of reaction of the alumina with the salt coated and/or by different distributions of the surface layer depending on the post-heating temperature. An increase in the post-heating temperature results in a considerable decrease in the retention time for all of the solutes investigated and a significantly improved peak shape. From a comparison of chromatograms, the salt-coated alumina adsorbents show the following characteristics for peak separation. The LiCl- and NaCl-coated alumina adsorbents gave good GSC separations of polychloro-substituted benzene isomers and *cis* and *trans* isomers of 2-olefins, whereas the KCl- and CsCl-coated alumina adsorbents gave good peak resolution of polychloro-substituted benzene isomers but very poor separations of *cis* and *trans* isomers of 2-olefins. The LiCl- and CsCl-coated alumina adsorbents resulted in somewhat broad and unsymmetrical peaks for all solutes investigated, whereas the NaCl- and KCl-coated alumina adsorbents yielded sharp and symmetrical peaks. Unfortunately, the results of the present study can only with difficulty be compared with those of other authors because of the different dispersions of the salts coated on the alumina surface. From our results, we conclude that the NaCl-coated alumina adsorbent is the most useful for practical GSC.

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