February, 1982] © 1982 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 55, 441—443 (1982) 441

Plasma Treatment of Packing Materials for Gas Chromatography. Diatomaceous Earth Coated with Squalane

Yukio Yamamoto,* Seiji Oka, and Koichiro Hayashi
The Institute of Scientific and Industrial Research, Osaka University, Yamadakami, Suita, Osaka 565

(Received July 9, 1981)

Commercially obtained column packings for gas chromatography, diatomaceous earth coated with 5% squalane, were treated with argon plasma by using a radiofrequency generator. It has been shown that the plasma treatment improves the chromatographic properties, in particular, reduces the tailing of aromatic hydrocarbon peaks. The effect of the plasma treatment has been attributed to the reduction of the support adsorptivity by the formation of inert coating on the support surface.

A growing interest has been arising in the application of plasma chemistry to surface treatment of solid materials.[1-3] An attempt has been made to apply inert gas plasma to the treatment of packing materials for gas chromatography, and the results of the preliminary experiments suggested that the argon plasma treatment of the packing such as diatomaceous earth coated with Apiezon L or squalane improves its chromatographic properties.[4] The effect has been attributed to the formation of inert coating on the support surface. The surface of diatomite supports is known to be covered with reactive silanol groups which cause tailing of chromatographic peaks, and several methods are used to reduce the activity of the supports.[5] It is expected that the argon plasma treatment of packings is effective for the reduction of the support adsorptivity. In the present study the effect of the plasma treatment of diatomaceous earth coated with 5% squalane was studied in some detail.

Expermental

Column packings, 60/80 mesh Chromosorbs W and P (non-acid washed) coated with 5% squalane, were obtained from Wako Pure Chemical Industry. The reactor used for the plasma treatment is shown in Fig. 1. The packing (about 4 g) was treated on a glass plate (9 cm diameter) in a bell jar with argon plasma at a pressure of 0.20 Torr (27 Pa). The power for the reactor was supplied by a radiofrequency generator operated at 13.56 MHz and an output of 50 W. After the treatment the packing was packed with tamping and vibration into a 1 m×3 mm i.d. stainless steel tube as well as the untreated packing. Before its use the column was conditioned overnight at 130 °C. The gas chromatography was carried out on a Hitachi gas chromatograph, Model 063, equipped with a flame ionization detector by injecting about 0.1 μl hydrocarbon mixtures. The flame ionization detector was substituted for a thermal conductivity cell detector when the retention time of oxygen was measured for determination of the adjusted retention times. The column was operated at 40 °C with a nitrogen flow of 30 ml/min. ESCA measurement of the support recovered from the packing by Soxhlet extraction was performed on a Du Pont ESCA 650 B electron spectrometer by employing a Mg $K\alpha_{1,2}$ photon source at 1253.6 eV.

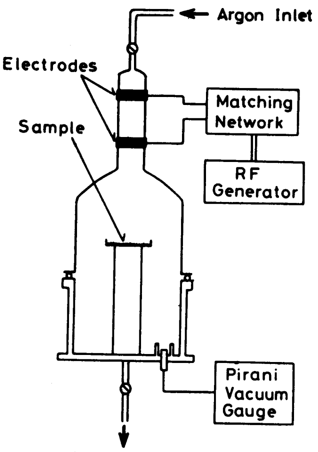

Fig. 1. Reactor used for the plasma treatment.

Results and Discussion

The effect of the argon plasma treatment of 60/80 mesh Chromosorb W (non-acid washed) coated with 5% squalane is shown in Fig. 2 where the chromatograms of a mixture of hexane, benzene, cyclohexane, heptane, toluene, ethylbenzene, and *o*- and *m*-xylenes on the untreated and 30 min treated packings are presented. It can be seen that the retention times of all the compounds and the tailings of the aromatic hydrocarbon peaks are reduced by the plasma treatment. Greater peak separation is also shown for benzene and cyclohexane on the treated packing. The changes in the adjusted retention times of the aliphatic and aromatic hydrocarbons are shown in Figs. 3 and 4, respectively, where the ratio of the adjusted retention time on the treated packing to that on the untreated packing, t'_{RO}/t'_{Rt}, is plotted against treatment time. A comparison of the figures shows that the retention times

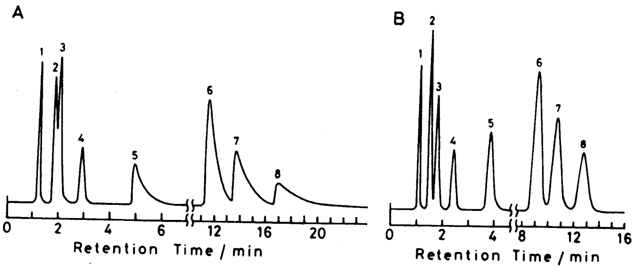

Fig. 2. Gas chromatograms on (A) untreated and (B) 30 min treated packings (Chromosorb W coated with 5% squalane) at 40 °C: the peaks are 1, hexane; 2, benzene; 3, cyclohexane; 4, heptane; 5, toluene; 6, ethylbenzene; 7, *m*-xylene; and 8, *o*-xylene.

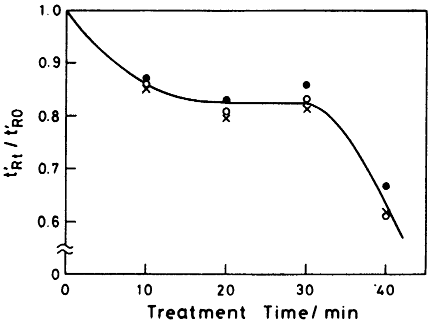

Fig. 3. Change in the adjusted retention times of aliphatic hydrocarbons: (○), hexane; (●), cyclohexane; and (×), heptane.

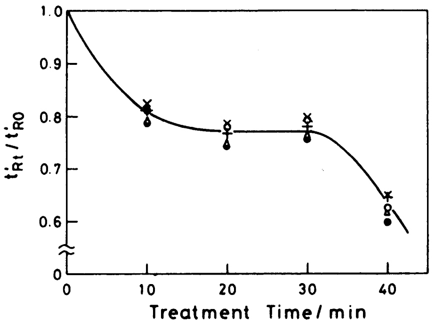

Fig. 4. Change in the adjusted retention times of aromatic hydrocarbons: (○), benzene; (●), toluene; (×), ethylbenzene; (△), *o*-xylene and (+), *m*-xylene.

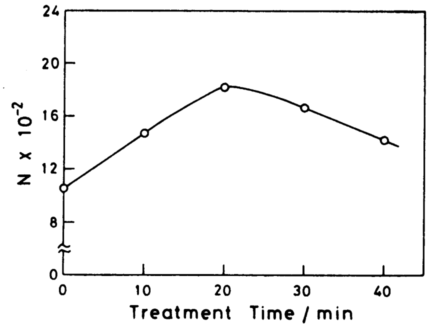

Fig. 5. Change in the number of theoretical plates (N).

of the aromatic hydrocarbons are reduced more than those of the aliphatic hydrocarbons by the plasma treatment. Figure 5 shows the change in the number of theoretical plates (N) by the plasma treatment, which was calculated from the peaks of ethylbenzene and *o*- and *m*-xylenes as $16(t_R/W_b)^2$, where t_R and W_b are the retention time and the peak width at base, respectively. The value attains maximum at around 20 min and then decreases by further treatment. The weight loss of the packing during the plasma treatment was too small to measure accurately, less than 0.4% up to a treatment time of 40 min.

In order to elucidate the modification of the packing by the plasma treatment the stationary liquids were extracted from the untreated and 20 and 40 min treated packings with tetrahydrofuran by using Soxhlet extractors and refluxing for 5 h, and then the recovered supports were dried under vacuum. The weight losses of the untreated and 20 and 40 min treated packings by the extraction were 4.9, 4.0, and 3.4%, respectively. Since the original packing has a liquid phase content of about 4.8% (5% relative to the support), the result means that the stationary liquid is almost completely extracted from the untreated packing but not from the treated packing, and the remaining component increases with increasing treatment time.

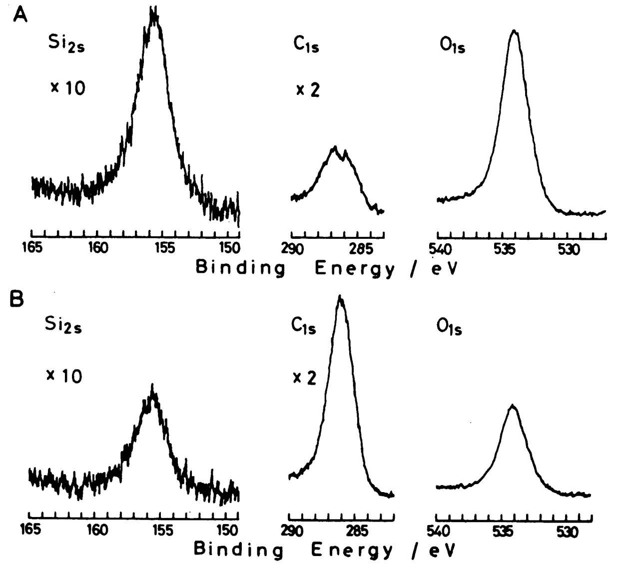

Fig. 6. ESCA Si_{2s}, C_{1s}, and O_{1s} peaks of supports recovered from (A) untreated and (B) 20 min treated packings.

ESCA measurement of the recovered supports was examined to obtain information about their surface compositions. Figure 6 shows the Si_{2s}, C_{1s}, and O_{1s} peaks of the ESCA spectra obtained for the untreated and 20 min treated packings. The C_{1s} peak is much larger for the treated sample than for the untreated sample, and the Si_{2s} and O_{1s} peaks arising from the diatomite support are reduced for the treated sample. The spectra demonstrate that the surface of the support recovered from the treated packing is covered with an organic component. On the other hand, the relative heights of the Si_{2s} and O_{1s} peaks are not affected by the plasma treatment, indicating that the surface composition of the support itself does not change.

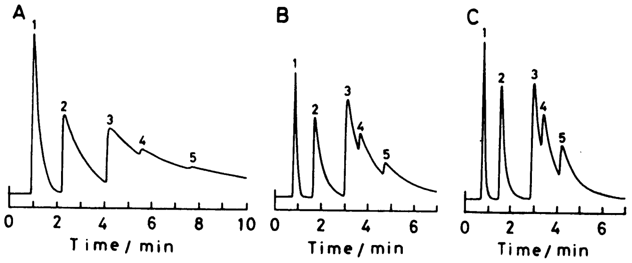

Fig. 7. Gas chromatograms on supports recovered from (A) untreated, (B) 20 min and (C) 40 min treated packings at 40 °C: The peaks are 1, benzene; 2, toluene; 3, ethylbenzene; 4, *m*-xylene; and 5, *o*-xylene.

The supports recovered from the packings were packed into the 1 m stainless steel tubes, and the columns were examined for gas chromatography. Figure 7 shows the gas chromatograms of a mixture of the aromatic hydrocarbons on the recovered supports. The retention times and tailings are reduced with increasing treatment time, suggesting that the adsorptivity of the support is reduced by the plasma treatment.

The untreated and treated packings were washed with carbon tetrachloride, and after filtration the carbon tetrachloride solutions of the stationary liquids were submitted to NMR spectrometry. There was no detectable difference in the spectra between the untreated and treated samples, and the spectra were identical with that of commercially obtained squalane. The result suggests that the soluble component of the stationary liquid of the treated packing remains unchanged.

On the basis of these results it can be considered that the plasma-induced reaction is restricted to the support surface and results in the formation of inert coating which is not extracted with tetrahydrofuran. The effect of the plasma treatment on gas chromatogram was shown to be more pronounced for the aromatic hydrocarbons than for the saturated aliphatic hydrocarbons. This is due to the fact that aromatic hydrocarbons have greater interaction with the surface silanol groups of the support than saturated aliphatic hydrocarbons.

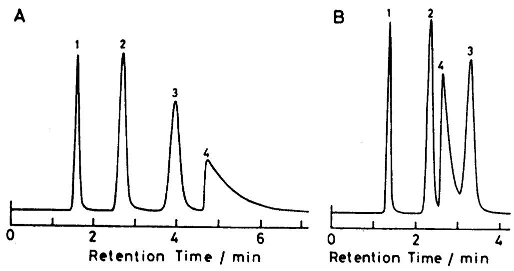

Fig. 8. Gas chromatograms on (A) untreated and (B) 20 min treated packings (Chromosorb P coated with 5% squalane) at 40 °C: the peaks are 1, hexane; 2, cyclohexane; 3, heptane; and 4, benzene.

The argon plasma treatment of the packing with another kind of support, 60/80 mesh Chromosorb P (non-acid washed) coated with 5% squalane, was examined by the same way to investigate the effect on the support adsorptivity. Figure 8 shows the gas chromatograms on the untreated and 20 min treated packings. On the untreated packing with Chromosorb P benzene is eluted later than heptane with a significant tailing, while on the untreated packing with Chromosorb W benzene is eluted faster than cyclohexane with a much smaller tailing (Fig. 2). It is known that Chromosorb P is more adsorptive than Chromosorb W because of the greater number of hydroxyl groups on the surface.[5] Therefore, the difference in the gas chromatograms between the untreated packings with Chromosorbs P and W can be explained by the great interaction of aromatic hydrocarbons compared with saturated aliphatic hydrocarbons. The result also demonstrates that the gas chromatograms are significantly affected with the support adsorptivity. On the other hand, on the treated packing with Chromosorb P benzene is eluted faster than heptane with a reduced tailing, indicating that the plasma treatment is effective for the reduction of the support adsorptivity.

Usually, the lower the column temperature, the greater is the tailing of gas chromatographic peaks. The results of the present study show that the plasma treatment makes it possible to use the packings at lower column temperature. Unfortunately, no information has been obtained about the chemical composition and formation mechanism of the insoluble component produced on the support surface. However, it seems reasonable to assume that the stationary liquid is converted to a highly crosslinked polymer on the support surface by the plasma treatment and the reaction is promoted by the reactive support surface.

This work was supported in part by Shimadzu Co. The authors wish to thank Mr. Hitoshi Yamada for his assistance in measuring the ESCA spectra.

References

1) M. Hudis, "Techniques and Applications of Plasma Chemistry," ed by J. T. Hollahan and A. T. Bell, Wiley-Interscience, New York, N. Y. (1974), p. 113.

2) H. Yasuda, *J. Macromol. Sci., Chem.*, **A10**, 383 (1976).

3) D. H. Reneker and L. H. Bolz, *J. Macromol. Sci., Chem.*, **A10**, 599 (1976).

4) Y. Yamamoto, S. Oka, and K. Hayashi, *Chem. Lett.*, **1981**, 221.

5) O. E. Schupp, III, "Gas Chromatography," ed by E. S. Perry and A. Weissberger, Interscience, New York, N. Y. (1968), p. 173.