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PLASMA TREATMENT OF PACKING MATERIALS FOR GAS CHROMATOGRAPHY

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Argon plasma treatment of packing materials, 25% Apiezon L on Chromosorb W and 5% Squalane on Chromosorb W, improved the gas chromatographic resolution. The liquid stationary phase was extracted from the treated and untreated Apiezon L packings, and pronounced modification was observed with the recovered support.

There has been much interest recently in application of plasma chemistry to surface treatment and modification of solid materials.[1] In the present study inert gas plasma was applied to the treatment of packing materials for gas chromatography, and the effect of the treatment on the gas chromatographic resolution was studied.

Commercially obtained packings were treated on a plate in a bell jar by 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 in an 1 m stainless steel tube (3 mm i.d.) as well as the untreated packing. Nitrogen was used as carrier gas at a flow rate of 30 ml/min for the gas chromatographic test.

The plasma treatment was examined with a packing, 25% Apiezon L on Chromosorb W (60-80 mesh) obtained from Gasukuro Kogyo Co., and the gas chromatography was carried out at 80°C using a mixture of benzene, toluene, ethylbenzene, and o- and m-xylenes. The columns were aged overnight at 180°C before the gas chromatography. Figure 1 shows the changes in the number of theoretical plates, N, and the retention volume by the treatment. The number of theoretical plates was calculated from the peaks of ethylbenzene and xylenes because the peaks of benzene and toluene were too sharp for the accurate calculation. The number of theoretical plates increases until 20 min of the treatment time. The relative retention volumes of the samples were not affected with the treatment, while the absolute retention volumes decreased; in the figure

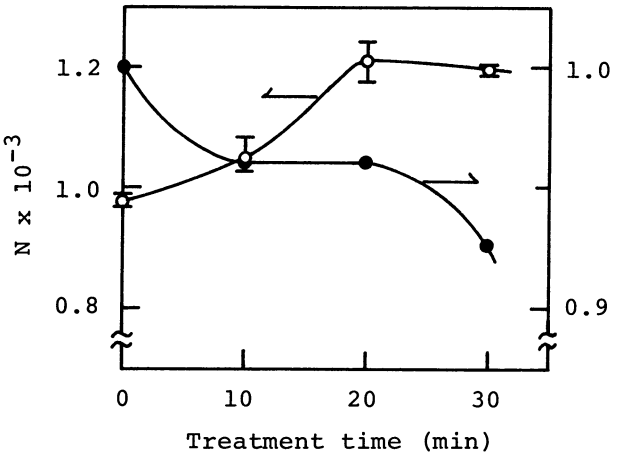

Fig. 1. Changes in the number of theoretical plates (O), and the retention volume (●); packing, 25% Apiezon L on Chromosorb W.

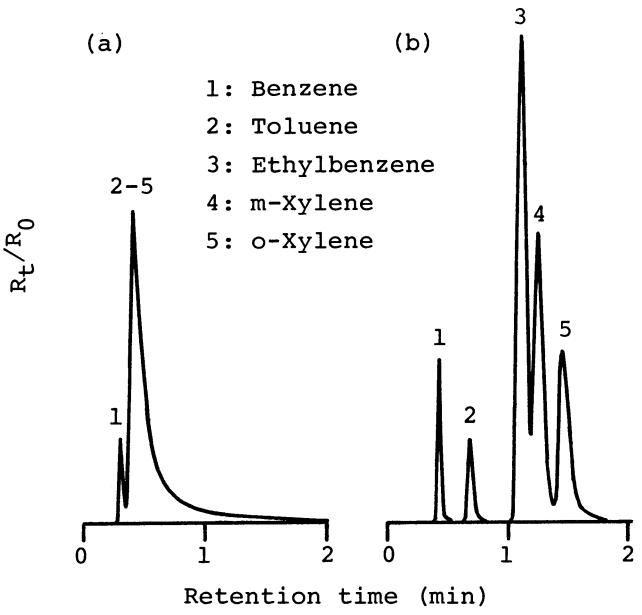

Fig. 2. Gas chromatograms on the supports recovered from (a) untreated and (b) treated packings at 80°C.

the ratio of the retention volume on the treated packing to that on the untreated packing, R_t/R_0, is plotted.

In order to obtain information about the effect of the plasma treatment on the packing the liquid stationary phase was extracted from the packing treated for 30 min and from the untreated packing with tetrahydrofuran by using Soxhlet extractors and refluxing for 5 h. The weight losses of the treated and untreated packings by the extraction were 17.1% and 19.6%, respectively.[2] The support of the treated packing was slightly colored yellow; the color was lighter than that of the original packing. On the other hand, the support of the untreated packing is white as well as commercially obtained Chromosorb W. The results show that the support of the treated packing is coated with the Apiezon L, which has been changed by the plasma treatment and cannot be extracted with tetrahydrofuran, while the liquid stationary phase is completely removed from the support of the untreated packing by the extraction. The supports recovered from the packings were packed in the 1 m stainless steel tubes, and the columns were tested by gas chromatography. Figure 2 shows the gas chromatograms of the aromatic hydrocarbons at 80°C. The support of the treated packing gives separated and sharp peaks in contrast to that of the untreated packing. The difference in the gas chromatograms also shows that the support is modified by the plasma treatment. The liquids recovered from the packings were submitted to NMR spectrometry, and there was no difference in the spectra between the treated and untreated samples, indicating

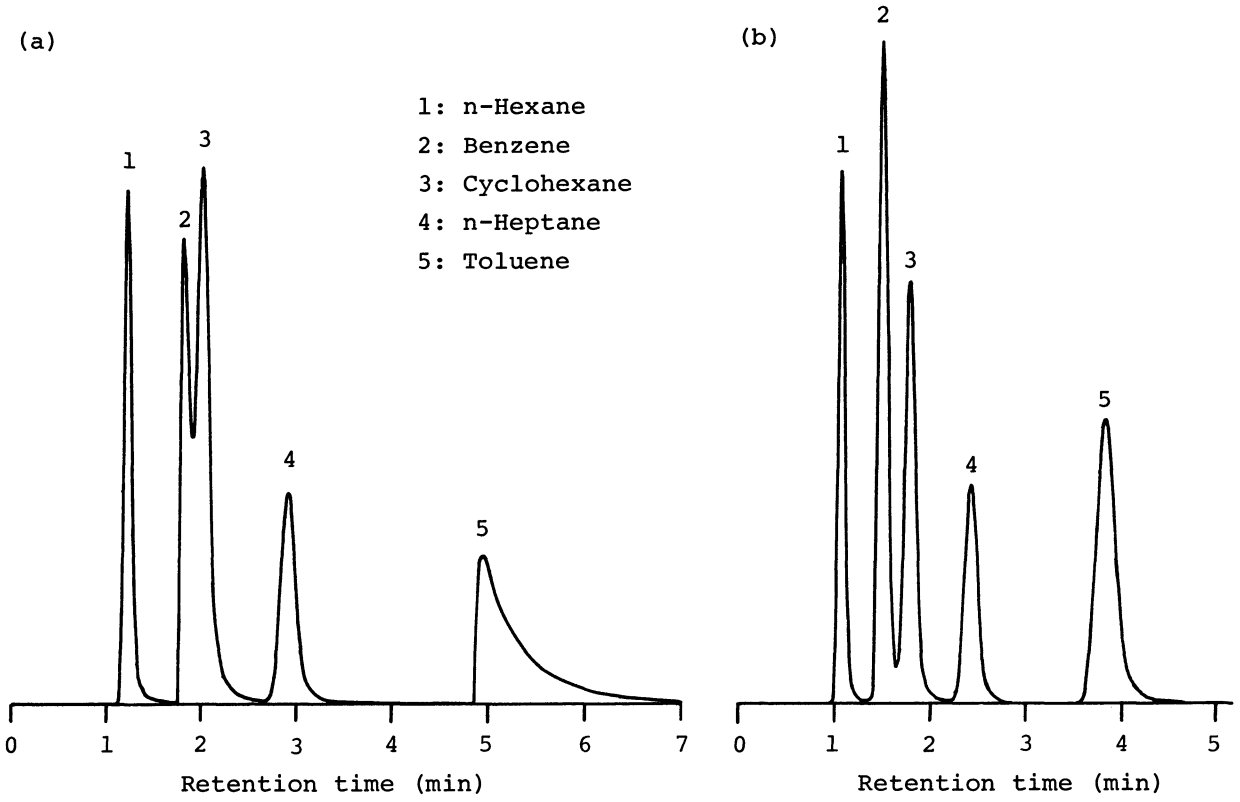

Fig. 3. Gas chromatograms on (a) untreated and (b) treated packings, 5% Squalane on Chromosorb W, at 40°C.

that the liquid stationary phase is hardly changed by the plasma treatment. On the basis of these results the effect of the plasma treatment on the gas chromatogram can be attributed to the modification of the surface of the support.

The plasma treatment of another packing, 5% Squalane on Chromosorb W (60-80 mesh) obtained from Wako Pure Chemical Industry, was examined by the same way. The columns packed with the packing treated by the argon plasma for 30 min and with the untreated packing were aged overnight at 130°C before the gas chromatography. Figure 3 shows the gas chromatograms of aliphatic and aromatic hydrocarbons at 40°C. By the treatment, the resolution is improved, and the retention volumes and the tailing of the peak of toluene are reduced. In the case of this packing the relative retention volumes of the individual compounds were affected with the treatment. The ratios of the retention volumes of the individual compounds on the treated packing to those on the untreated packing were n-hexane, 0.88; benzene, 0.82; cyclohexane, 0.89; n-heptane, 0.84; and toluene, 0.77; the effect on the retention volumes of the aromatic compounds are remarkable compared with the aliphatic compounds. It seems reasonable to assume that the effect of the plasma treatment is due to the reduction of the adsorptivity of

the support.

It has been well established that the surface of the diatomite support is covered with adsorptive silanol groups which cause tailing of chromatographic peak.[3] It appears that the plasma treatment results in the reduction of the support adsorptivity by the inert coating arising from the liquid, Apiezon L or Squalane. Plasma etching and polymerization have been applied to preparation of glass capillary columns for gas chromatography by Masada and his coworkers.[4] However, we feel that the present study is the first example of plasma treatment of packing materials. The plasma treatment of other packing materials is under investigation.

This work was supported in part by Shimadzu Corporation which offered the apparatus for the plasma treatment.

References and Note

1) See for example, (a) M. Hudis, "Plasma Treatment of Solid Materials", in "Techniques and Applications of Plasma Chemistry", J. R. Hollahan and A. T. Bell, Eds., Wiley-Interscience, New York, N. Y. (1974); (b) H. Yasuda, J. Macromol. Sci.-Chem., A10, 383 (1976); (c) D. H. Reneker and L. H. Bolz, J. Macromol. Sci.-Chem., A10, 599 (1976).

2) The packing contains 20 wt% liquid (25 wt% based on the support), and the extraction is considered to be completed within 5 h since the liquid was not extracted by the prolonged reflux. The weight loss of the packing by the plasma treatment was less than 0.1% and can be neglected.

3) See for example, O. E. Schupp III, "Gas Chromatography", "Technique of Organic Chemistry", Vol. XIII, E. S. Perry and A. Weissberger, Eds., Interscience, New York, N. Y. (1968), p. 173.

4) Y. Masada, K. Hashimoto, T. Inoue, Y. Sumida, T. Kishi, and Y. Suwa, J. High Resolution Chromatogr. & Chromatogr. Commun., 2, 400 (1979).

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