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# GAS CHROMATOGRAPHIC BEHAVIOUR OF CHEMICALLY BONDED MICROPARTICULATE SILICA

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SUMMARY

The gas chromatographic behaviour of different kinds of chemically bonded microparticulate silica was investigated. The chemically bonded stationary phase YWG-CN with $d_p$ = 10–15 $\mu$m showed a column efficiency ($2.4 \cdot 10^4$ theoretical plates per metre) and mass transfer coefficient ($5.8 \cdot 10^{-5}$ sec) comparable to those for microparticulate silica. The surface polarity was also determined and compared with those of silica and graphitized carbon black (GCB). The order of polarity was YWG-10 (silica) > YWG-CH > YWG-CN > YWG-NR$_4$ > YWG-NH$_2$ > YWG-OR > GCB. Some examples of separations are given.

INTRODUCTION

A good column packing for gas chromatography (GC) must have good column efficiency, permeability and selectivity. A satisfactory microparticulate packing in high-performance GC (HPGC) must, however, also have excellent mechanical strength. Many types of packing, such as molecular sieves, alumina, silica gel, charcoal, diatomaceous earth and polymers, have been widely used in many fields. Of these, alumina and silica gel have good mechanical strength as microparticles and are satisfactory for use in HPGC. Microspherical silica gel not only has a high mass transfer rate and good permeability, but also a column efficiency comparable to that in high-performance liquid chromatography[1,2], and is therefore attractive for HPGC development.

Unfortunately, for many analytical purposes one must use stationary phases with polarities that silica gel does not possess. The chemically bonded silicas developed recently may have different polarities depending on their bonded surfaces, and can be used for various purposes such as the analysis of oxygen-containing compounds and of hydrocarbons.

The purpose of this work was to evaluate the chromatographic behaviour of the chemically bonded microparticulate silicas prepared by the Tienjin Second Chemical Reagent Plant and to widen their use in HPGC.

We investigated the column efficiency, mass transfer rate and relative surface polarity and its effect on the selectivity.

EXPERIMENTAL

*Apparatus*
A home-made chromatograph equipped with a flame-ionization detector and two types of columns (10 cm × 2 mm, and 15 cm × 2 mm I.D. stainless-steel tubes) were used.

*Packings*
YWG-7 (7 ± 2 $\mu$m), YWG-10 (10–15 $\mu$m) and YWG-20 (20–25 $\mu$m) micropar-ticulate silica produced by the Tsingdao Ocean Chemical Plant and YWG-CN, YWG-NH$_2$, YWG-NR$_4$, YWG-OR ($d_p$ = 10–15 $\mu$m) and YWG-CH ($d_p$ = 10–15 and 44–62 $\mu$m) chemically bonded silica prepared by the Tienjin Second Chemical Reagent Plant were used. The physico-chemical properties of their surfaces are shown in Table I.

TABLE I

PHYSICO-CHEMICAL PROPERTIES OF THE SURFACES OF THE CHEMICALLY BONDED MICROPARTICULATE SILICAS

Original support, microparticulate silica, with a specific surface area of about 300 m$^2$/g and a pore diameter of about 100 Å.

| Commercial name | Organic functional groups on surface | Organic coverage (%, w/w) |
|---|---|---|
| YWG-CH | $\equiv$Si–C$_{18}$H$_{37}$ | 10 |
| YWG-CN | $\equiv$Si–(CH$_2$)$_2$CN | 8 |
| YWG-NH$_2$ | $\equiv$Si–(CH$_2$)$_3$NH$_2$ | 9 |
| YWG-NR$_4$ | $\equiv$Si–(CH$_2$)$_3$-R$_3$N | 7 |
| YWG-OR | $\equiv$Si–OC$_{12}$H$_{25}$ | – |

RESULTS AND DISCUSSION

*Column efficiency*
The results show that the column efficiency of chemically bonded micropartic-ulate silica is about the same as that of silica, except that of YWG-NH$_2$, which is slightly lower. We determined the HETP values at various linear flow-rates. The (HETP)$_{min.}$ value of the chemically bonded YWG-CN, for example, is about 41 $\mu$m, corresponding to 2.4 · 10$^4$ theoretical plates per metre with carbon dioxide as the carrier gas. Fig. 1 shows a plot of $\bar{H}$ versus $\bar{u}$.

In order to compare the column efficiencies of chemically bonded stationary phases with that of the original silica, a plot of $H_{min.}$ versus particle size ($d_p$) is shown in Fig. 2. The good straight line demonstrates that both chemically bonded micropar-ticulate silica and microparticulate silica have similar good column efficiencies.

*Mass transfer rate*
The uniformity and reproducibility of high-performance chromatographic col-umns packed with microparticles by the unbalanced-density slurry technique were
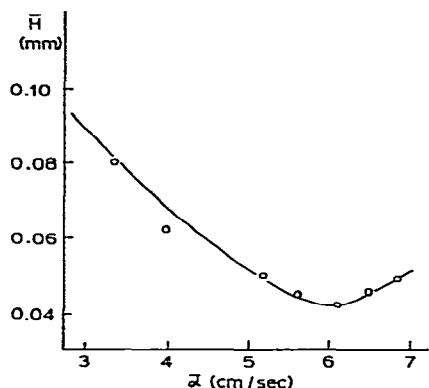
Fig. 1. Plot of $\bar{H}$ against $\bar{u}$ using a 100 × 2 mm I.D. column packed with YWG-CN. Carrier gas, carbon dioxide.
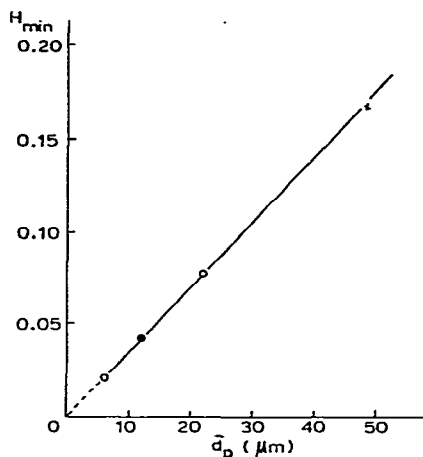
Fig. 2. Plot of $H_{min}$ versus $\overline{d_p}$. Carrier gas, carbon dioxide; column temperature, ambient. Column packings: ●, YWG-CN; ×, YWG-CH; ○, silica.

demonstrated previously[1]. The overall mass transfer coefficient was less than $10^{-5}$ sec when $7 \pm 2$ $\mu$m silica was used as the packing with carbon dioxide as the carrier gas. Using the same experimental conditions and methods, we also determined the mass transfer coefficient of the chemically bonded YWG-CN (10–15 $\mu$m) by plotting $\bar{H}\alpha_0$ versus $\alpha_0^2$ (Fig. 3). The value obtained (5.8 · $10^{-5}$ sec) is very suitable for HPGC.
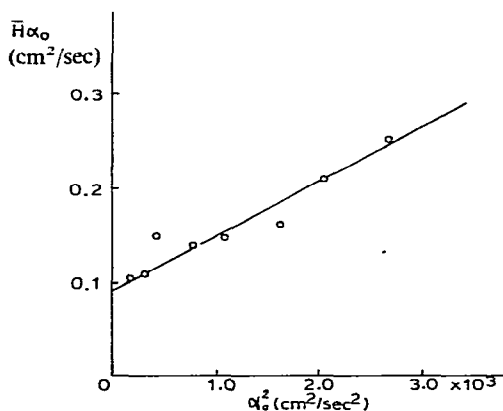
Fig. 3. Plot of $\bar{H}\alpha_0$ versus $\alpha_0^2$. Packing, YWG-CN (10–15 $\mu$m); carrier gas, carbon dioxide; column temperature, ambient.

*Surface polarity*

The surface polarity of chemically bonded silica was determined by GC[3,4] using the solute pairs ethylene–ethane, propylene–propane and butadiene–butane, then the ratios of the retention times for these three pairs for each type of chemically bonded stationary phase were determined under the same operating conditions. Fig. 4 shows the plots of retention time ($t'_r$) ratios against number of carbon atoms ($N_c$), and
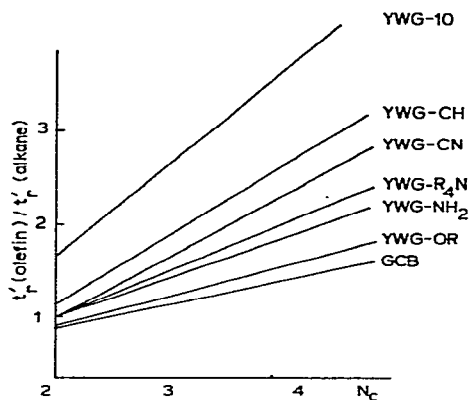
Fig. 4. Comparison of surface polarities of chemically bonded stationary phases with that of silica and GCB.

indicates that the surface polarity determined by GC is located between that of graphitized carbon black (GCB) and silica. In these experiments GCB and silica were taken as non-polar and polar standards, respectively.

Table II lists the values of $p$ (the surface polarity for the supports relative to silica). The $p$ value was calculated from the ratio of the relative retention times of the pairs on the packings divided by that on silica.

TABLE II

RELATIVE SURFACE POLARITIES OF DIFFERENT SUPPORTS

| Support | $p_1{}^{\star}$ | $p_2{}^{\star}$ | $p_3{}^{\star}$ |
|---------|------|------|------|
| GCB | 0.54 | — | 0.36 |
| YWG-OR | 0.55 | 0.46 | 0.46 |
| YWG-NH$_2$ | 0.60 | 0.52 | 0.55 |
| YWG-NR$_4$ | 0.60 | 0.51 | 0.57 |
| YWG-CN | 0.60 | 0.55 | 0.66 |
| YWG-CH | 0.70 | 0.70 | 0.73 |
| YWG-10 | 1.00 | 1.00 | 1.00 |

$\star$ $p_1$, $p_2$ and $p_3$ were determined using solute pairs with $N_c = 2$, 3 and 4, respectively.

It can be seen clearly from both Fig. 4 and Table II that the order of surface polarities is YWG-10 (silica) > YWG-CH > YWG-CN > YWG-NR$_4$ > YWG-NH$_2$ > YWG-OR > GCB. This result shows that the surface polarity of chemically bonded stationary phases does not agree with the order of polarity according to the functional groups bonded on the surface of the supports. The results are also different from those obtained by Al Thamir *et al.*[5].

*Examples of separations of mixtures*

The separation of aromatics from alkanes, olefins from alkanes and especially
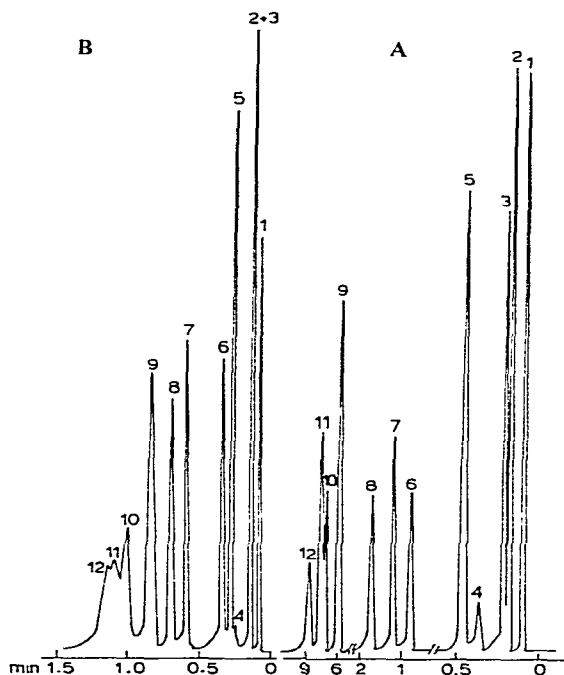
Fig. 5. Separation of gaseous hydrocarbons with hydrogen as carrier gas. Column packings: (A) YWG-CH; (B) YWG-CN. Column temperature, ambient. Column dimensions, 150 × 2 mm I.D. Peaks: 1 = methane; 2 = ethane; 3 = ethylene; 4 = acetylene; 5 = propane; 6 = propylene; 7 = isobutane; 8 = n-butane; 9 = butene-1; 10 = trans-butene-2; 11 = cis-butene-2; 12 = butadiene.
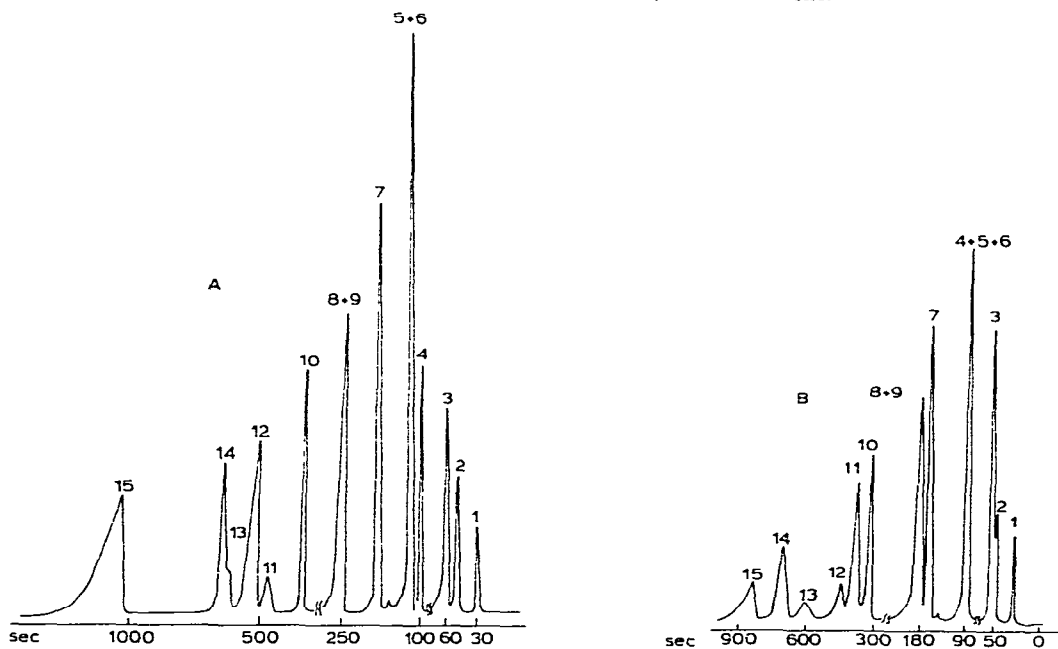


Fig. 6. Separation of two $C_5$–$C_{10}$ hydrocarbons mixtures with hydrogen as carrier gas. Column packings: (A) YWG-CH; (B) YWG-CN. Column dimensions, 150 × 2 mm I.D.; temperature, 100°C. Peaks: 1 = n-pentane; 2 = n-hexane; 3 = hexene-1; 4 = n-heptane; 5 = heptene-1; 6 = benzene; 7 = n-octane; 8 = toluene; 9 = octene-1; 10 = n-nonane; 11 = m-xylene; 12, 13 = unknowns; 14 = n-decane.

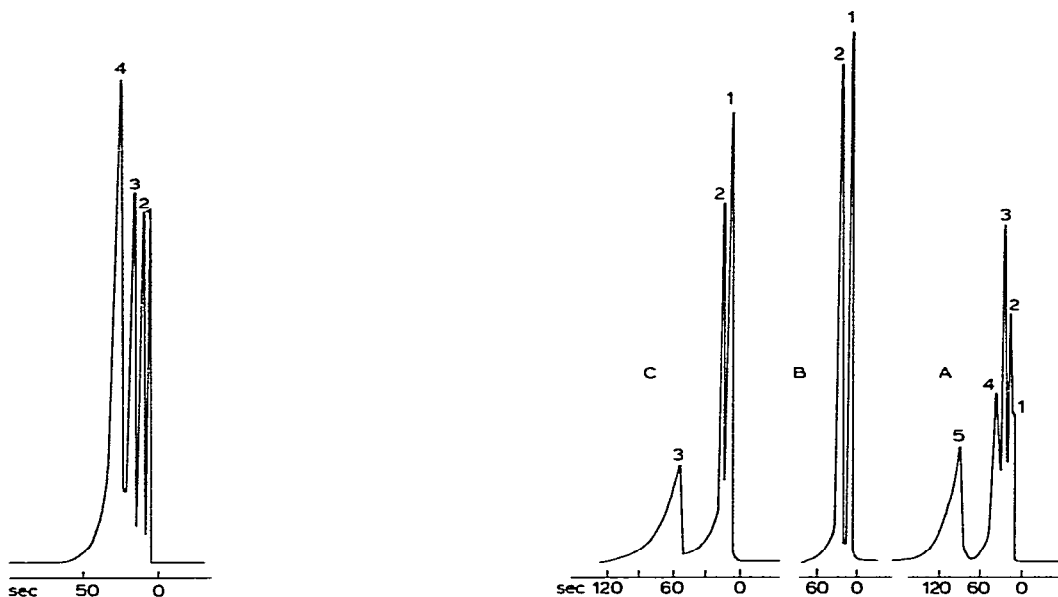Fig. 7. Separation of aromatic hydrocarbons with carbon dioxide as carrier gas. Column dimensions, 100 × 2 mm I.D.; packing, YWG-CN; temperature, 180°C. Peaks: 1 = benzene; 2 = toluene; 3 = *m*-xylene; 4 = trimethylbenzene.

Fig. 8. Separation of oxygen-containing compounds with carbon dioxide as carrier gas. Column dimensions, 100 × 2 mm I.D.; packing, YWG-CN; temperature, 180°C. Peaks: (A) 1 = methanol; 2 = ethanol; 3 = propanol; 4 = isobutanol; 5 = amyl alcohol; (B) 1 = ethyl acetate; 2 = amyl formate; (C) 1 = acetone; 2 = methyl ethyl ketone; 3 = cyclohexanone.

ethylene from ethane depends mainly on the surface polarity of the supports in gas–solid chromatography. The separations of mixtures of $C_1$–$C_4$ gaseous hydrocarbons (Fig. 5) and $C_5$–$C_{10}$ hydrocarbons (Fig. 6) show different resolutions as a result of the different surface polarities of the chemically bonded YWG-CH and YWG-CN. In the separation of aromatic hydrocarbons (with low polarity) and oxygen-containing compounds (intermediate or high polarity), symmetrical peaks were obtained, as shown in Figs. 7 and 8, respectively. All of the results show the advantages of using chemically bonded stationary phases.

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