

Deactivation and modification of non-porous silica surfaces with polysiloxanes in capillary chromatography

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DEACTIVATION AND MODIFICATION OF NON-POROUS
SILICA SURFACES WITH POLYSILOXANES
IN CAPILLARY CHROMATOGRAPHY

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Abstract Deactivation of fused silica capillary columns and vitreous silica surfaces with polymethylhydrosiloxanes at temperatures between 240°C and 360°C is investigated by gas chromatography and solid state ^{29}Si NMR on a non-porous model substrate. Further modification of deactivated silica surfaces with a stationary phase containing polymethyloctadecylsiloxane is optimized and evaluated.

INTRODUCTION

The use of polymethylhydrosiloxanes (PMHS) for deactivation of the inner wall of fused silica (f.s.) capillary columns in recent years^{1,2} yielded substantial improvements in non-polar surface deactivation. Although very effective deactivation with PMHS was obtained, the nature of the deactivating film inside the f.s. capillaries is still largely unknown. Here we describe parallel deactivation with PMHS inside f.s. capillaries and on Cab-O-Sil, a vitreous silica, which serves as a model substrate for f.s. capillaries, allowing spectrometric surface characterization. The use of fumed vitreous silica in combination with solid state NMR has proved to be a powerful tool for the study of surface moieties after silylation³⁻⁵. Combined, ^{29}Si magic angle spinning (MAS) NMR and ^{29}Si cross-polarization magic angle spinning (CP-MAS) NMR techniques provide significant information on the chemical properties, the relative amounts, the nature and the mobilities of the anchored auto cross-linked PMHS chains at the silica surface after silylation. The results of the measurements of silylated

Cab-O-Sil can be matched with the retention behavior and peak shape of sensitive test compounds for remaining siloxane/silanol activity and basic or acid adsorption^{1,2} on likewise deactivated f.s. capillaries. After optimal deactivation, at 290°C for about 4 hours, the f.s. capillary column wall shows no interaction with critical test compounds. Cab-O-Sil, deactivated under identical conditions as the f.s. capillaries revealed additional information on the structure of the deactivating film.

In capillary column preparation practice deactivation is followed by further modification with a suitable stationary phase. In this study we concentrate on a new stationary phase, suitable for fast gas chromatography (GC), capillary super-critical fluid chromatography (SFC) and eventually open tubular liquid chromatography (OTLC), when applied in narrow-bore columns (inner diameter ≤ 50 μm). Our attention is focussed on a relatively thick, stable and uniform stationary phase film containing polymethyl-octadecylsiloxanes (PMOS). Interactions with the PMOS deactivating film underneath are improved when dried Cab-O-Sil is added to the coating. A relatively high ratio of the cross-linking agent benzoyl peroxide improves the stability of the stationary phase as well. Again, model studies with solid state ^{29}Si NMR gave information on chemical properties, rigidity and stability of the stationary phase and the interactions with the PMOS deactivating layer.

BACKGROUND

Capillary f.s. columns in chromatography typically have inner diameters between 200 and 530 μm . At present only thin film capillary SFC and fast GC columns are available with inner diameters down to 50 μm . However, because of the extremely low specific surface area of these non-porous capillaries solid state NMR and other spectroscopic analysis techniques can not be applied for surface characterization. Therefore, a non-porous fumed vitreous silica, Cab-O-Sil, with a large enough specific surface area and solid particles with a typical diameter of about

10 nm is chosen as a model substrate for surface deactivation and modification. One should consider, however, that for f.s. capillaries deactivation and modification is performed at the inner wall, while for Cab-O-Sil the outer surface of the particles is used, see Figure 1.

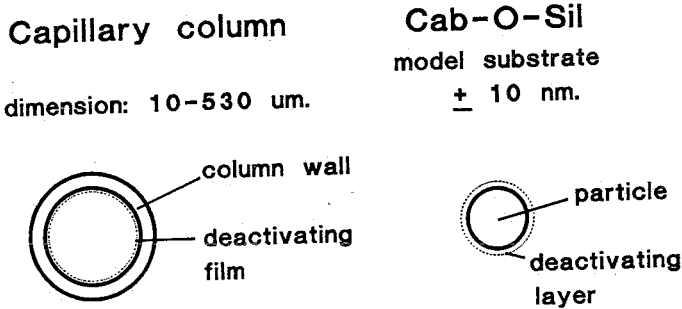
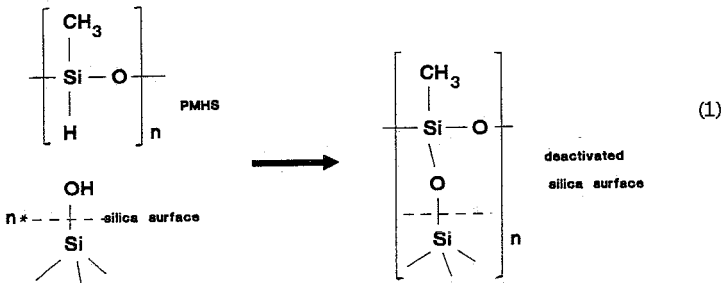


FIGURE 1. Comparison of the two non-porous silica surfaces used in this study.

Deactivation of the active silanol and siloxane groups at non-porous silica surfaces with PMHS proceeds through condensation:



This reaction proceeds rapidly at moderate temperatures around 290°C. If some physisorbed water is present at the surface, this interferes by hydrolysis of the silicon-hydrogen bond and intra- and intermolecular cross-linking of PMHS can occur^{2,7,8}. The presence of water causes also extra silanol activity which should

diminish by the deactivation of the siliceous surface. In this study the silylation temperature, the film thickness and the influence of physisorbed water at the surface are parameters which have been considered explicitly.

Subsequent to optimal PMHS deactivation, modification with a thick film coating containing PMODS was performed. To improve interactions with the PMHS deactivating film underneath the PMODS is cross-linked with the radical initiating benzoyl peroxide, 14 (w/w)%. Dried Cab-O-Sil, 14(w/w)%, is added. Both benzoyl peroxide and C-O-Sil improved the stability of the stationary phase. The ratios are the result of our optimization of the coating procedure of the deactivated capillaries (see below) and the study of interactions with the deactivating film and stability with solid state NMR.

EXPERIMENTAL AND RESULTS

Materials

The PMHS material PS 122 (50% Si-H, $\eta = 85\text{cS}$, liquid) and the PMODS material PS 130 (50% Si-C₁₈, $M_w = 28000\text{ g.mol}^{-1}$, $M_n = 7000\text{ g.mol}^{-1}$, solid) were obtained from Petrarch Systems Inc. (Bristol, PA, USA). The amount of methylhydrodisiloxysilane (D₂H) groups in PMHS as determined by HR liquid ²⁹Si NMR was 96% ± 1%. The only other significant signal in the ²⁹Si NMR spectrum was assigned to trimethylsiloxysilane (M₁) end groups and is found less than 5% in this sample. This indicates only a small amount of short linear polymers is present in PS 122. A GC-MS analysis of PS 122 on a thin film apolar column, showed a large dispersion of both cyclic and linear polymethylhydro-siloxanes. The amount of methylocta-decyldisiloxysilane (D₂C₁₈) in the PMODS determined by solid state ²⁹Si CP-MAS NMR was 95% ± 2%. Here also some M₁ end groups, about 3%, together with unreacted D₂H, about 2%, were found. For an approximate quantitative analysis with ²⁹Si CP-MAS NMR and secondary information on the mobility of the polymer PMODS chains a cross-polarization contact time variation curve (see below) is

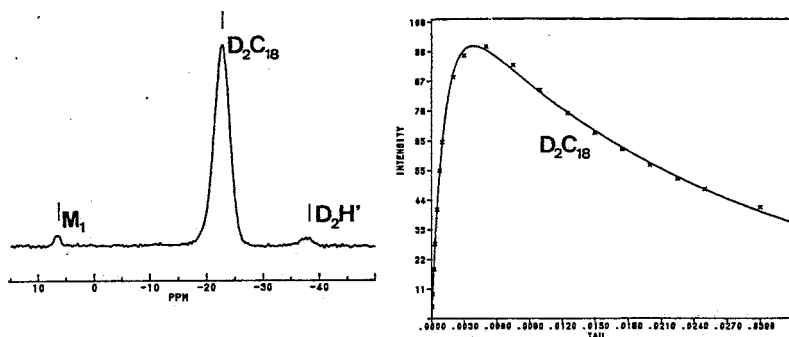


FIGURE 2. Solid state ^{29}Si CP-MAS NMR spectrum of the pure PMODS polymer with the contact time variation curve of the D_2C_{18} groups. $N_s = 960$, pulse interval time: 7.5 s., acquisition time: 50 ms., contact time spectrum: 5ms.

depicted as well in Figure 2. The specific surface area of Cab-O-Sil grade M5, after rehydroxylation and drying, was measured with BET: $202 \pm 5 \text{ m}^2\text{g}^{-1}$. A value of $200 \text{ m}^2\text{g}^{-1}$ for the rehydroxylated (model substrate) and the dried Cab-O-Sil (mixed with the coating) was used in this study. The benzoyl peroxide was obtained from Aldrich (Aldrich-Europe, Beerse, B). The solvents used were all analytical grade from Merck AG (Darmstadt, FRG) except for the demineralized, deionized water, which was obtained with a Milli-Q System (Millipore Corp., Bedford, MA, USA).

Deactivation and Modification

Fused silica capillaries

Four pieces of capillaries with a length of ca. 18 m. were hydrothermally pretreated and coated dynamically with a 1 (v/v)% PS122 solution in n-pentane as described by Hetem et al.⁸. The calibrated film thickness after deactivation is about 10 nm. Deactivation was performed at different temperatures and reaction

times, subsequently the capillaries were rinsed with dichloromethane and conditioned at 290°C for 30 min. purging with helium. The deactivated capillaries are evaluated using a double column system: a thick film separation column (24 m.* .32 mm. I.D., CP-sil 5cb.), showing as little adsorption as possible, connected with one of the deactivated capillaries^{3,8}. In this way the deactivation

TABLE 1. Test mixture for evaluation of deactivated capillaries.

Elution order on CP-Sil 5 CB	Compound	Symbol	Concentration ($\mu\text{g ml}^{-1}$ cyclohexane)	Activity marker for
1	Decane	10	119.0	—
2	1-Octanol	C ₈ -OH	112.4	Exposed siloxane bonds, weak
3	2,6-Dimethylphenol	DMP	118.3	Exposed basic sites, strong
4	Undecane	11	116.6	—
5	2,5-Dimethylaniline	DMA	114.7	Exposed acid silanol, strong
6	Dodecane	12	114.4	—
7	1-Aminododecane	Am	116.4	Shielded acid silanol, weak
8	Tridecane	13	107.8	—
9	Nicotine	Nic	121.0	Acid silanol, weak
10	Tetradecane	14	128.4	—

can be evaluated with a mixture of sensitive test compounds, listed in Table 1. This allows observation of peak shapes, measurements of inner wall polarity by means of retention index shifts and quantitative comparison of column activity, expressed in chromatographic peak area, for differently deactivated capillaries. Chromatograms of the deactivated capillaries with the reference/separation column are shown in Figure 3. Typically 1 to 3 ng. for each test component was injected on the double column evaluation system. A quantitative analysis of the results is reported elsewhere⁸.

After the optimization of the deactivation procedure a few capillary columns (ca.5 m. long * 50 μm .I.D.) were deactivated with PMHS under optimal conditions, 290°C for 2 hours, and tested. These columns were subsequently coated with various PMODS/dried Cab-O-Sil-M5/benzoyl peroxide mixtures in tetrahydrofuran (THF)/diethylether (DEE), 50:50, at a temperature of 55°C by solvent evacuation under reduced pressure. After successful evacuation

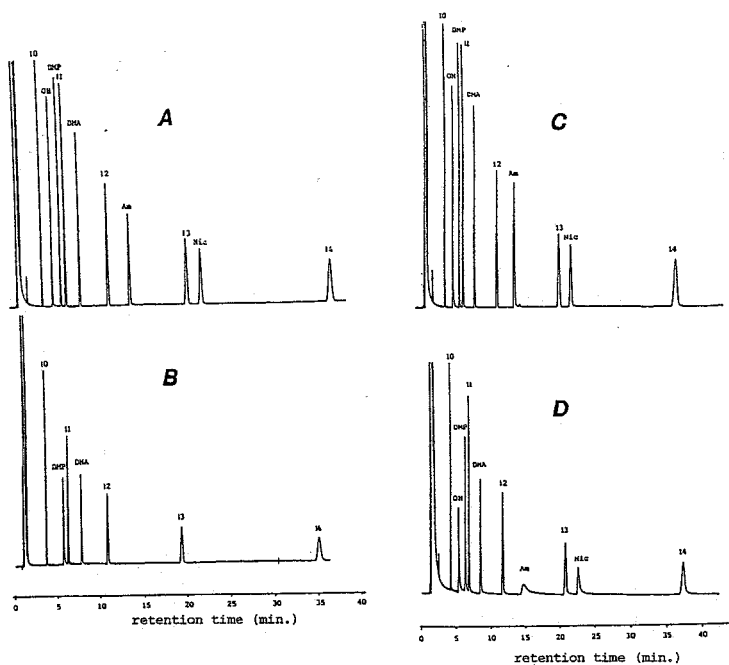


FIGURE 3. Representative chromatograms of the thick film reference column (A), an untreated capillary (B), an optimally deactivated capillary (C) and a capillary deactivated under non-optimal conditions (D). Test conditions: helium carrier gas, isothermal operation at 110°C . For peak identifications of the test mixture, see Table 1.

the columns were dried and subsequently cross-linked at 140°C for 2 hours with helium purge and further conditioned at 200°C for 15 hours. Optimization of this coating procedure was carried out using different stationary phase component ratios and stationary phase volumes. A final stationary phase component ratio of 72(w/w)% PMODS, 14(w/w)% dried Cab-O-Sil and 14(w/w)% benzoyl peroxide was found optimal for stationary phase volumes between 2% and 6% of the total column volume.

Cab-O-Sil particles

The Cab-O-Sil M5 was pretreated by ignition at 720°C and

rehydroxylated as described before^a. The Cab-O-Sil was dried further over phosphorus pentoxide in a vacuum dessicator for several weeks. The dried Cab-O-Sil was coated with an equivalent of 0.98 g. and 0.20 g. per gram resulting in a "thick film" layer of 5 nm. and a "thin film" layer of 1 nm. respectively. To this end, the PMHS was dissolved in n-pentane 10 (v/v)% and added to the required amount of Cab-O-Sil. Subsequent silylation progressed in flame sealed quartz glass reaction ampouls, as described elsewhere^a. The Cab-O-Sil was deactivated at temperatures between 240 and 360°C. After silylation, the deactivated Cab-O-Sil was washed twice with dichloromethane and dried overnight in a vacuum oven at 110°C. The thickness of the deactivating film was checked by carbon content analysis. With these samples various solid state ²⁹Si NMR measurements were carried out in order to obtain information about the chemical properties, the nature and mobility of the deactivating film at the siliceous surface.

A batch of optimally deactivated Cab-O-Sil, 290°C/8 hours, with a film thickness of 3nm. was coated with a second layer of 3 nm. containing PMODS. To this end, an identical coating mixture as mentioned above, was solved in THF/DEE (50:50) and added to the PMHS deactivated Cab-O-Sil. The solvent was evaporated under slightly reduced pressure at 55°C. The PMODS coated Cab-O-Sil was dried and cross-linked in a glass roar, 10 cm.* 4.6 mm.I.D., under helium flushing at 140°C for 2 hours and conditioned overnight at 200°C. As reference the pure coating mixture was cross-linked identically.

Solid state ²⁹Si NMR measurements

Solid state ²⁹Si NMR spectra were obtained with a CXP 300 spectrometer (Bruker, Karlsruhe, FRG) at 59.63 MHz. All samples were spun at 3.5 KHz. using alumina or zirconia rotors of the standard Bruker double bearing type. The siloxane/silane notation, ²⁹Si chemical and substituent induced shifts included in PMHS deactivation are depicted in **Figure 4**. From the 5 nm.PMHS deactivated Cab-O-Sil samples ²⁹Si MAS NMR spectra were obtained with a pulse interval time of 10s. Typically 256 free induction

decays (fid's) were accumulated and no line broadening was applied.

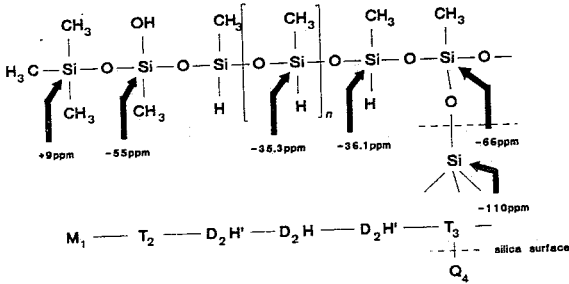


FIGURE 4. Siloxane/silane notation, ^{29}Si NMR chemical and substituent induced shifts most relevant for the PMHS deactivation study.

The spectra of Cab-O-Sil samples 1 to 4 are depicted in Figure 5. The shape of the narrow signal points out that the methylhydro-

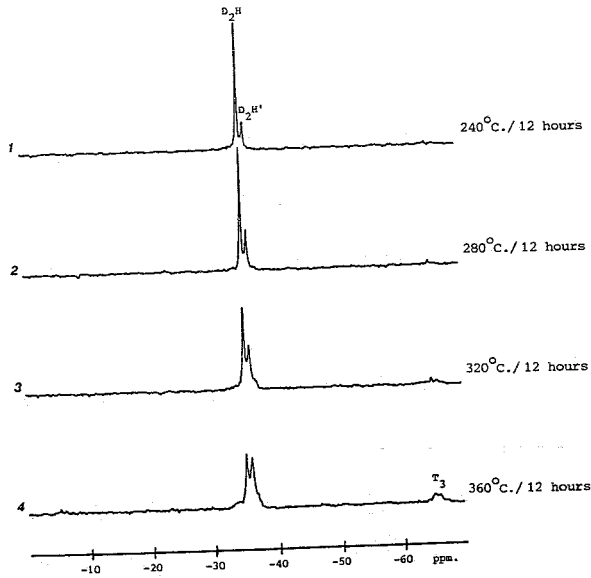


FIGURE 5. Solid state ^{29}Si MAS NMR spectra of thick film PMHS deactivated Cab-O-Sil samples.

disiloxysilane units (D_2H and D_2H') mainly belong to long mobile polymer chains anchored at the silica surface. The D_2H group at -35.3 ppm. has two unreacted neighbour groups, whereas the D_2H' group with a chemical shift at -36.1 ppm. has one or perhaps two T_3 groups on the α -position⁷. This T_3 group is responsible for intra- and intermolecular cross-linking of the polymer chains or surface attachment at the silica. From the 1 nm. FMHS deactivated Cab-O-Sil samples ^{29}Si CP-MAS NMR spectra were obtained using a contact time of 15 ms. The pulse interval time applied was 5 s. The spectra of Cab-O-Sil samples 5 to 8 are depicted in **Figure 6**.

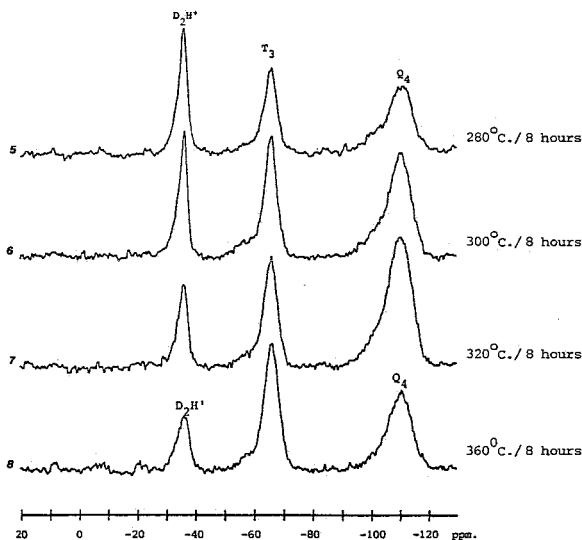


FIGURE 6. Solid state ^{29}Si CP-MAS NMR spectra of thin film PMHS deactivated Cab-O-Sil samples.

These samples demonstrate a structure of the siloxane moieties which is quite different from the thick film deactivated Cab-O-Sil samples. The long polymer methylhydrodi- siloxysilane chains are obviously degraded. The remaining methylhydrodisiloxysilanes (D_2H') are anchored to the surface via T_3 groups. The broad D_2H' signal

indicates a rather rigid thin deactivating film. Cross-polarization experiments, under the Hartmann-Hahn conditions¹⁰, with variable contact times show the transfer efficiency of magnetism between two nuclei involved. The cross-polarization dynamics, obtained by simulating the experimental curves with appropriate time constants, yield significant information regarding the mobilities of the sample in the 10^2 Hz. to 10^6 Hz. range¹¹. In this study contact time variation experiments between ^1H and ^{29}Si nuclei are performed.

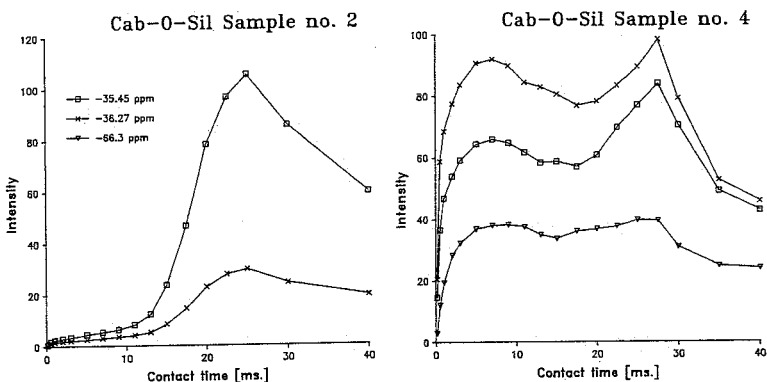


FIGURE 7. Contact time variation curves and chemical shifts for PMHS deactivated Cab-O-Sil samples 2 and 4.

From the the 5 nm. PMHS deactivated Cab-O-Sil samples 2 and 4, cross-polarization experiments with variable contact times, ranging from 0.1 to 40 ms., were applied, see Figure 7. After optimal deactivation with PMHS and subsequent PMODS coating, again cross-polarization experiments with variable contact times were performed. The contact time (CT) curve and the spectrum of the cross-linked PMODS (3 nm.) stationary phase on Cab-O-Sil deactivated with PMHS (3 nm.) is shown in Figure 8. Identically cross-linked bulk PMODS stationary phase showed a quite similar CT-curve.

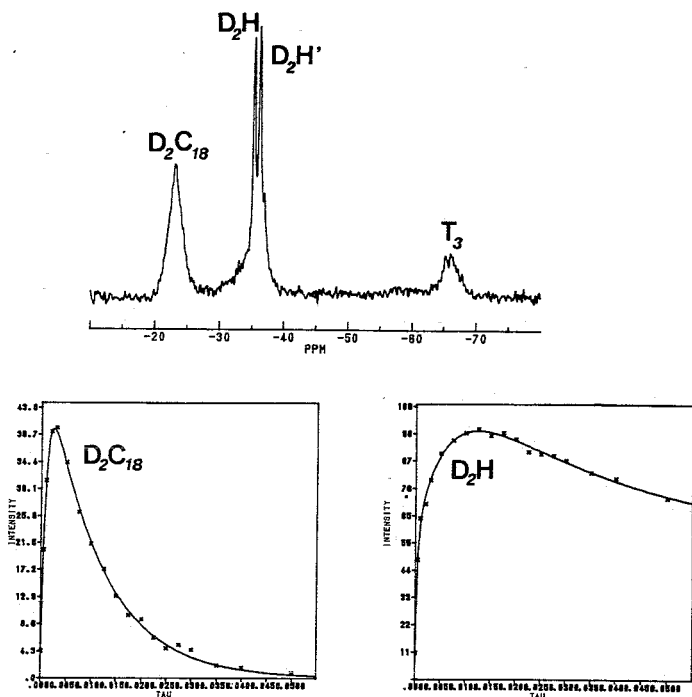


FIGURE 8. Solid state ^{29}Si CP-MAS NMR spectrum of the crosslinked stationary phase containing PMODS on PMHS deactivated Cab-O-Sil, with the contact time variation curves of D_2C_{18} and D_2H groups present on the substrate.

DISCUSSION

It was shown above with solid state ^{29}Si NMR that the natures of the films on Cab-O-Sil after deactivation with PMHS layers of 1 and 5 nm differ considerably. For thick film deactivation only slight degradation and cross-linking of PMHS polymers occurs. With increasing temperature the ratio between D_2H and $\text{D}_2\text{H}'$ groups at the surface decreases. Only a relatively small amount of T_3 groups, most likely at or close to the silica surface, is formed

with silylation temperatures above 320°C. The CT-curves of Cab-O-Sil sample 2, depicted in Figure 7., indicates also that mobile polymethylhydrosiloxane chains are still present after silylation at 280°C. The maximum intensity for the signals in the -35 ppm. region was observed for a contact time of ca. 27 ms, although already small signals were obtained with contact times between 1 and 10 ms. Therefore, the deactivating film can be described as two layers: a dense cross-linked network near the surface anchored through T₃ groups, only a few mono-layers thick and longer mobile, slightly cross-linked D₂H and D₂H' polymer chains attached to this rigid layer and protruding upwards, see Figure 9. These chains play a role in the anchoring of stationary phases during radical

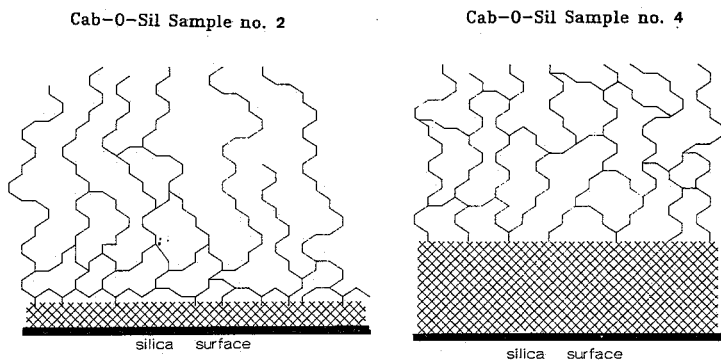


FIGURE 9. Models of the structure of the deactivating film after silylation of Cab-O-Sil samples 2 and 4.

induced cross-linking. The total number of T₃ cross-linking groups is very small. The CT-curves of Cab-O-Sil sample 4, silylated at 360°C, demonstrate at least two distinct maxima at contact times of ca.7 and 27 ms, indicating that two coherent methylhydrodi-siloxysilane systems are present in the deactivating film: mobile slightly cross-linked D₂H and D₂H' polymer chains, similar to silylation at 280°C, on top of a rigid layer with many immobile small-chain segments, intensely cross-linked, anchored to the surface, see Figure 9. After thin film deactivation the PMHS

polymers are degraded and almost equal amounts of D_2H' and T_3 groups are formed. Mobile D_2H polymer chains are not present at the surface. With increasing silylation temperatures the amount of D_2H' groups decreases in favour of T_3 groups. These T_3 groups form a rigid, dense cross-linked layer with a thickness of several monolayers, anchored to the surface.

In any comparison between results obtained with model chemistry and actual deactivation of f.s. columns as judged with GC, the thickness of the deactivating film plays a crucial role. With f.s. columns the thickness of the deactivating film, calibrated according to Bartle^{12,20}, was between 10 and 30 nm. Consequently, one should compare these f.s. capillaries with thick-film silylated Cab-O-Sil samples. After silylation of Cab-O-Sil with PMHS for several hours at 280-290°C., with a stoichiometry corresponding with a film thickness of 5 nm, an anchored network was obtained close to the surface of Cab-O-Sil with only slight cross-linking. Of the total methylhydrodi-siloxysilane units attached to the surface, only ca.20% occupied α -position with respect to surface attachment or cross-linking after silylation. It proved difficult to detect the T_3 groups by ²⁹Si MAS NMR, mainly because of their relatively low concentration of ca.5-10%. In spite of this apparently low conversion of D_2H groups to T_3 groups which attach the polymer chains tightly to the silica surface, the surface was adequately covered and deactivated, as shown by the GC experiments. Also silicon-hydride groups remaining in the chains apparently do not interfere with the elution of the appropriate test components in GC experiments.

In this study we observed that methylhydrodisiloxy-silanes show a high reactivity towards silanol groups, particular to those which are Brønsted acids. In our opinion, it seems that one of the main advantages of silylating agents containing silicon hydride moieties is connected with the small (Van der Waals) dimensions of these groups, rather than with their high intrinsic reactivity. Further, cross-linking of the chains near the surface, although of low overall concentration, provides additional surface screening. The optimum deactivating film exhibits excellent thermal stability

and solvent resistance.

Subsequent PMODS coating of optimally PMHS deactivated Cab-O-Sil showed a changed D_2H to D_2H' ratio, relatively more D_2H' groups were found after stationary phase cross-linking and conditioning. This indicates chemical interactions between the deactivating film (D_2H) and the stationary phase on top. Compared with the pure PMODS polymer the CT-curve of the cross-linked D_2C_{18} points to decreased mobility. A quite similar CT-curve was determined for D_2C_{18} groups in cross-linked bulk stationary phase. The mobility of the D_2C_{18} groups in the stationary phase is decreased by dense cross-linking with benzoyl peroxide and hardly influenced by interaction with the PMHS film or the substrate. The CT-curve for D_2H groups in the deactivating film though, is changed by coating and cross-linking with the PMODS stationary phase. The maximum in the CT-curve shifts from *ca.*27 ms. for optimally deactivated Cab-O-Sil to *ca.*13 ms. for deactivated and coated Cab-O-Sil. The mobility of the D_2H groups is decreased clearly.

The PMODS stationary phase used as a coating in deactivated f.s. capillary columns showed good thermal stability and solvent resistance. The amount of stationary phase as determined from the GC capacity factors, did not decrease after conditioning at 200°C and intensive solvent rinsing with various organic solvents

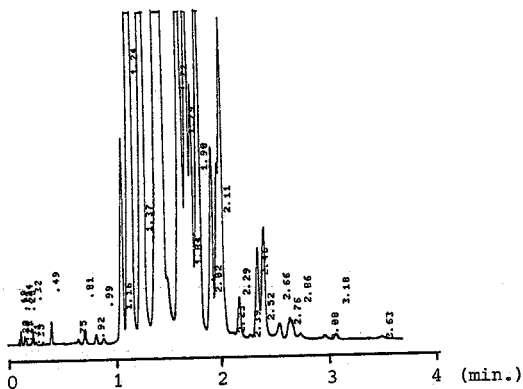


FIGURE 10. Fast GC chromatogram of a mixture of aromatic compounds separated with a 50 μ m I.D.* 4 m. column, stationary phase volume 5(v/v)%, isothermal run 110°C.

or with high density CO₂. Capillary columns with 50 μ m I.D. and stationary phase volumes between 2(v/v)% and 6(v/v)% were prepared. Separation efficiencies of 12000 plates per meter were obtained with a 50 μ m column. An example of the applications feasible with the columns evaluated above, is a fast GC analysis of aromatic compounds as shown in Figure 11. Characterization with the test mixture in Table 1 showed little adsorption for some of the sensitive compounds, probably due to poor deactivation of the dried Cab-O-Sil mixed with the stationary phase. Future studies will be aimed at reduction of such adsorption. Furthermore, the chromatographic evaluation, especially with SFC will be performed.

ACKNOWLEDGEMENT

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