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A CP-MAS NMR Study of Some Deactivation Methods in Capillary Gas Chromatography

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Silylation

Summary

The effect of temperature, water content, and the type of reagent on the silylation of fused silica capillaries was studied by ^{29}Si and ^{13}C CP-MAS NMR. Fumed silica (Cab-O-Sil M5), which is essentially a highly dispersed vitreous quartz with a surface comparable to that of fused silica capillary columns, was selected as a model material.

Hexamethyldisilazane (HMDS) and 1,2-diphenyl-1,1,3,3-tetra-phenyldisilazane (DPTMDS), which were used as silylation reagents, yielded trimethyl- and dimethylphenylsilyl surface groups respectively at lower temperatures ($< 350^\circ\text{C}$ and $< 250^\circ\text{C}$ respectively). At higher temperatures, increasingly more dimethylsilyl groups are formed, with the silicon bound to two oxygen atoms. This process occurs for DPTMDS at a considerably lower temperature than for HMDS. The formation of silyl groups on the surface and the disappearance of hydroxyl groups are followed independently. The ^{13}C NMR and GC-MS of the reaction products showed that with DPTMDS, the formation of two Si-O-Si links is accompanied by a loss of phenyl groups rather than of methyl groups.

After the Cab-O-Sil had been dried over P_2O_5 , the formation of these double links occurred for HMDS only at temperatures above 460°C and for DPTMDS at 400°C . Thus we concluded that water supplies oxygen atoms for double Si-O-Si links (possibly crosslinks) necessary for efficient deactivation. This may explain the less successful silanization of fused silica capillaries because their water content is lower than that of glass capillaries.

1 Introduction

Deactivation of glass capillary columns by means of high temperature silylation at 300°C with hexamethyldisilazane (HMDS) was introduced by *Welsch et al.* [1]. *Grob* [2], in an extensive study on experimental conditions, found an optimum temperature of 400°C and introduced another reagent, diphenyltetramethyldisilazane (DPTMDS). For

glass capillary columns this high temperature silylation is applied to previously leached and dehydrated columns, a large excess of reagent is used, and the reaction is usually carried out for 4–16 hours at 400°C . Columns treated this way are deactivated very well for polar compounds.

A number of points, however, remain unclear:

– Compared to other silylation methods, the reaction is carried out at the rather high temperature of 400°C . In the preparation of bonded phases for HPLC, for example, the silylation reactions are often carried out in refluxing toluene.

– *Grob* introduced DPTMDS, hoping to obtain better temperature resistance of the deactivation and better wettability of the column wall. He also used mixtures of HMDS and DPTMDS [3,4]. The difference between these two reagents was not very clear and the expected improvement in wettability not very pronounced. Only the use of tetraphenyldimethyldisilazane and triphenylsilylamine improved the wettability [5].

– We have used high temperature silylation successfully in the deactivation of glass capillary columns. When we applied the same procedure to fused silica columns, less satisfactory results were obtained. This seems to be general experience, for in practice most workers deactivate fused silica columns by silylation with octamethylcyclotetrasiloxane (D4) [6–10] introduced by *Stark et al.* [11] or by polysiloxane degradation (PSD or “baking”) [9,10,12,13] introduced by *Schomburg et al.* [14].

Therefore, we think that deactivation methods warrant further study. Unfortunately, the interior of a capillary column is hardly accessible for surface analysis techniques other than chromatographic ones. The result of a surface reaction must therefore necessarily be judged from the analysis of the reaction products or from the chromatographic behavior of the column. Moreover, neither the correlation between chemical nature of the wall, solute interaction, and chromatographic peak shape nor the influence of the chromatographic parameters (length of

column, linear velocity of carrier, temperature or temperature ramp, concentration, internal diameter, film thickness etc.) on the peak shape are clearly established.

Modern techniques of surface analysis in glass technology require far larger surface areas than a section of a capillary column can provide. Therefore, one is bound to use model materials e.g. glass sheets [15,16]. Moreover, these techniques provide information on the atomic composition of the surface layers rather than on the nature of the organic moieties of modified surfaces.

A powerful tool for the characterization of such species is cross-polarization magic-angle-spinning (CP-MAS) NMR of ^{13}C and ^{29}Si nuclei: Maciel and coworkers [17,18] characterized modified silica gels with CP-MAS NMR and more recently, they also quantitatively studied the dehydration and rehydration of silica gels [19] and the reactivities of surface silanol groups with HMDS [20].

Owing to the cross-polarization procedure, only ^{29}Si (or ^{13}C) nuclei near a spatially fixed proton contribute to the NMR signal. As protons in silicas are usually only present in $=\text{SiOH}$ or $=\text{Si}(\text{OH})_2$ groups on the surface, ^{29}Si CP-MAS NMR in practice functions as a surface analysis technique.

In connection with an earlier study on the leaching of glass [21], we attempted to record ^{29}Si CP-MAS NMR spectra of glass powders or glass fibers. Even small glass particles of 25 μm would have too low a specific surface area. Smaller particles do not allow leaching to be carried out as is usual in column technology.

Therefore we decided not to use glass or to study leaching and we selected a fumed silica as a model compound because:

- its specific surface area is about 130–400 m^2/g , which makes it amenable for CP-MAS NMR [22,23].
- its primary particles are nonporous spheres (diameter 5–25 nm), consisting essentially of vitreous quartz (SiO_2 content > 99.8%), which compares well with the surface of fused silica columns.
- contrary to glass, it can be heated above 700°C, sufficient to remove any internal “water”.

A fumed silica (Cab-O-Sil M5) was used previously by Boksányi *et al.* [24] in an extensive study on the reactions of trialkylsilanols with silica surfaces.

2 Experimental

2.1 Materials

The Cab-O-Sil M5 (Cabot Corp., Tuscola, Ill., USA) was a gift from Heybroek & Co's Handels Maatschappij N. V. Amsterdam. The specific surface area of grade M5 is, according to the manufacturer, $200 \pm 25 \text{ m}^2/\text{g}$. A value of $200 \text{ m}^2/\text{g}$ was used in this work.

Hexamethyldisilazane (bis(trimethylsilyl)amine) was obtained from Pierce Chemical Co., Rockford, Ill., USA, (specially purified grade) and 1,3-diphenyl-1,1,3,3-tetramethyldisilazane was obtained from Fluka, Buchs, Switzerland (purum). Other solvents were all analytical grade from Merck, Darmstadt, FRG.

2.2 Pretreatment of Cab-O-Sil

The Cab-O-Sil M5 was heated in an electric oven in a porcelain crucible to 720–750°C, in order to remove “water” inclusions according to Taylor and Hockey [25]. After cooling, the Cab-O-Sil was rehydrated by refluxing it with ultra pure water for five hours. Because Cab-O-Sil forms a suspension and cannot be filtered, the water was removed in a rotary evaporator. The rehydrated sample was dried overnight in a vacuum oven at 110°C. Part of the Cab-O-Sil was dried further over P_2O_5 in a desiccator for several weeks.

2.3 Silylation of Cab-O-Sil

Cab-O-Sil (ca. 0.2–0.5 g) was placed in a thick-walled test tube (I.D. 7.5 mm, O.D. 12 mm, length 20 cm) made from Duran glass and weighed. Then the open end of the tube was drawn out in a flame to a smaller bore (ca. 4 mm O.D.). (If absolute dryness was required, the tube was placed again for some weeks in a desiccator with P_2O_5). The tube was evacuated and filled with nitrogen to atmospheric pressure. The required amount of reagent was added with a syringe. The tube was evacuated (for volatile reagents the tube was meanwhile cooled in dry ice) and sealed. After sealing the ampoule typically had a volume of 5 ml. For reactions at and above 400°C tubes of vitreous quartz were used (10 mm I.D., 12 mm O.D., length 20 cm). After sealing its volume was about 8 ml.

The required amount of silylating reagent was calculated following Boksányi [24]: A fully hydrated silica has a surface concentration of about 7.8 $\mu\text{mol}/\text{m}^2$ SiOH. Stöber [26] attained a surface concentration of 4.7 $\mu\text{mol}/\text{m}^2$ $-\text{OSi}(\text{CH}_3)_3^*$ after reaction with $(\text{CH}_3)_3\text{SiCl}$, and Boksányi *et al.* attained the same value with R_3SiOH .

Therefore we used 10 μmol of reagent per square meter of Cab-O-Sil (taking a specific surface of $200 \text{ m}^2/\text{g}$ this is 322 mg of HMDS per gram of Cab-O-Sil or 571 mg DPTMDS per gram of Cab-O-Sil), which is more than 4 times this maximum amount. However, this is less than the 0.12–0.20 mg/cm^2 of HMDS that Godefroot *et al.* [27] used for glass columns (3.200–5.300 times the stoichiometric amount).

After sealing, the ampoules were wrapped in aluminum foil, placed in a well ventilated oven and heated to the required temperature for 16 hours.

*Note: Throughout this paper $-\text{OSi}$, $(-\text{O})_2\text{Si}$ etc. are abbreviations for $(=\text{SiO})\text{Si}$, $(=\text{Si-O})_2\text{Si}$, etc.

Table 1**Experimental conditions.**

Sample no. not dried	dried over P ₂ O ₅	Reagent	Reaction Temperature (°C)
1		–	25
2		–	200
3		–	300
4	24	–	350
5		–	390
6		–	500
7		HMDS	25
8		HMDS	200
9		HMDS	350
10		HMDS	385
11		HMDS	400
	25	HMDS	430
	26	HMDS	460
	27	HMDS	480
12	28	HMDS	500
13		DPTMDS	25
14		DPTMDS	200
15	29	DPTMDS	300
16	30	DPTMDS	350
17		DPTMDS	400
	31	DPTMDS	425
	32	DPTMDS	450
18		HMDS/DPTMDS 1:1	400
19		10:1	400
20		100:1	400
	33	1:1	350 (72 h)

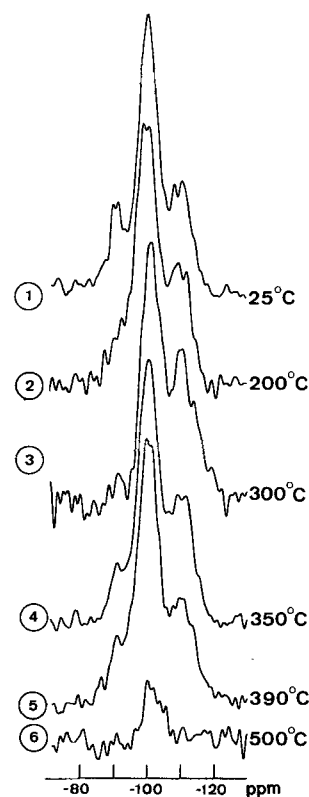
Reheated samples	Original reagent	Reheating temperature
21 (from 7)	HMDS	400°C
22 (from 13)	DPTMDS	400°C
23 (from 26)	HMDS	500°C

After reaction the ampoules were opened and the contents washed twice with toluene and twice with methanol (the solvents can easily be removed by suction, because after silylation the Cab-O-Sil does not form a suspension). The Cab-O-Sil was dried in an oven at 80° and then overnight in a vacuum oven at 110°C.

After recording the NMR spectrum, in some cases an already modified Cab-O-Sil sample was heated again in an evacuated ampoule. **Table 1** lists the various Cab-O-Sil samples.

2.4 NMR Measurements

The ²⁹Si- and ¹³C CP-MAS NMR spectra were obtained on a Bruker CXP 300 spectrometer at 59.63 MHz and at 75.48 MHz, respectively. The samples were spun at ca. 3.8 kHz using Delrin (for ²⁹Si NMR) or boron nitride (for ¹³C NMR)

**Figure 1**

²⁹Si NMR spectra of Cab-O-Sil samples heated to the indicated temperatures without a reagent in a closed, evacuated ampoule. (The encircled numbers refer to the sample nos. in Table 1.)

Andrew type rotors. Single contacts were used with contact times of 2 ms (²⁹Si) or 5 ms (¹³C). Pulse interval times were 1 s (²⁹Si) or 3 s (¹³C NMR). Typically, 20,000 to 60,000 fid's were accumulated in 1k data points, zero-filled to 8k prior to Fourier transformation. The spectral width was 20 kHz.

3 Results and Discussion

Originally the reactions took place using Cab-O-Sil not dried over P₂O₅ after rehydration, but left exposed to the air for several weeks. Such a sample may contain 10–20% of water. Thermogravimetry showed that the bulk of this water is lost at temperatures below 110°C. Only 0.5–0.9% (w/w) is lost gradually between 110° and 700°C, for which the loss of water from SiOH groups can account. This means that the bulk of the water is only physisorbed.

3.1 Blanks

To study the effect of heating alone on the Cab-O-Sil, a series of NMR spectra (**Figure 1**) was recorded of Cab-O-Sil samples heated without a reagent in a closed evacuated ampoule (sample nos. 1–6 in Table 1). Three ²⁹Si NMR

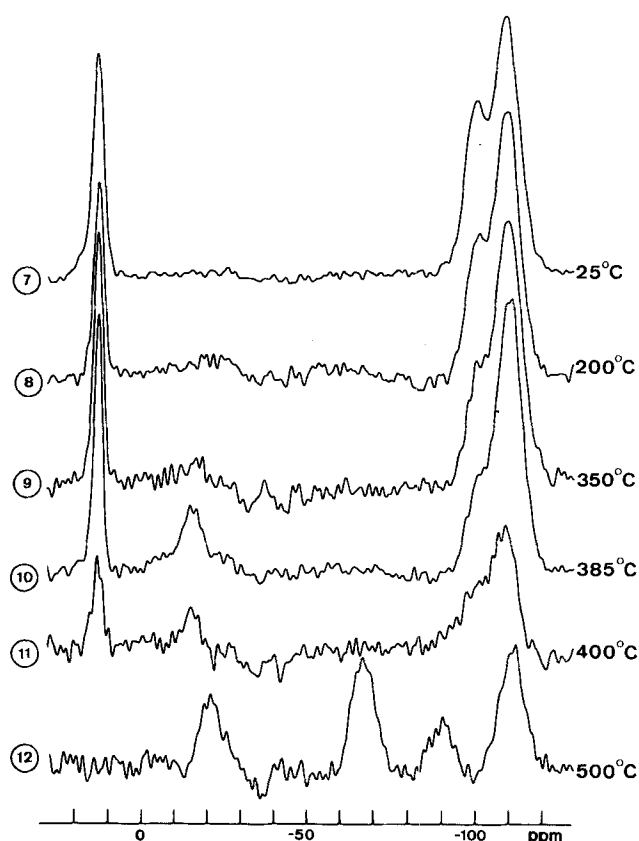


Figure 2
 ^{29}Si NMR spectra of Cab-O-Sil samples silylated with HMDS at the indicated temperatures. (The encircled numbers refer to the sample nos. in Table 1.)

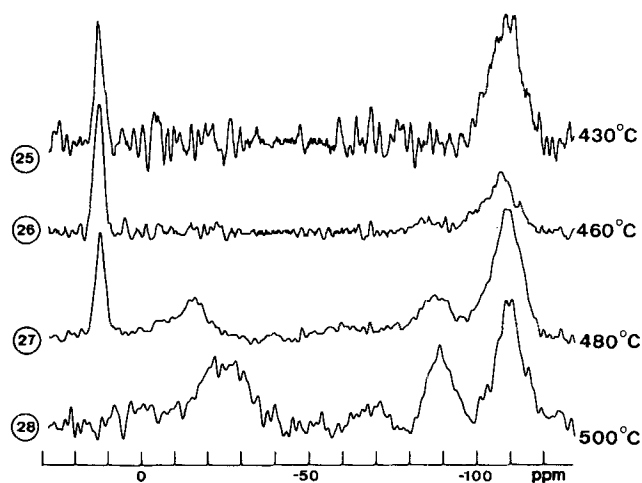
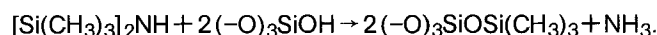


Figure 3
 ^{29}Si NMR spectra of Cab-O-Sil samples dried over P_2O_5 , and silylated with HMDS at the indicated temperatures. (The encircled numbers refer to the sample nos. in Table 1.)

signals are discernable: $(-\text{O})_2\text{Si}(\text{OH})_2$ at -92 ppm, $(-\text{O})_3\text{SiOH}$ at -101 ppm, and $(-\text{O})_4\text{Si}$ at -110 ppm. There are no significant differences between these spectra, although one would expect that two neighboring $\equiv\text{SiOH}$ groups would split off water and form a $\equiv\text{Si-O-Si}\equiv$ bridge. The temperatures were probably not high enough here to produce irreversible changes of such a kind, and any water formed, which cannot escape from the closed ampoules, reacts again with the $\equiv\text{Si-O-Si}\equiv$ bridges upon cooling.

3.2 Reaction with HMDS

Samples 7–12 (Table 1) were prepared with HMDS and ^{29}Si NMR spectra were recorded (Figure 2). Up to reaction temperatures of 350°C three signals were found: at $+12$ ppm $-\text{OSi}(\text{CH}_3)_3$, at -101 ppm $(-\text{O})_3\text{SiOH}$, and at -110 ppm $(-\text{O})_4\text{Si}$. The relative intensities of the two latter signals change as a consequence of the disappearance of $(-\text{O})_3\text{SiOH}$ groups and the concomitant formation of $(-\text{O})_4\text{Si}$ groups during the silylation. This agrees with the expected reaction



At 385°C , however, a peak at -16 ppm of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ appears, and at 500°C a peak at -66 ppm of $(-\text{O})_3\text{SiCH}_3$.

In the spectra of Figure 2, as compared to Figure 1, the signal of the geminal $(-\text{O})_2\text{Si}(\text{OH})_2$ has disappeared, but the signal of the mono $(-\text{O})_3\text{SiOH}$ is still present. This is in agreement with the established greater reactivity of $(-\text{O})_2\text{Si}(\text{OH})_2$ groups. Only at 385°C and above is the -101 ppm signal reduced.

From this we conclude that the reaction of HMDS with Cab-O-Sil only leads to the formation of $-\text{OSi}(\text{CH}_3)_3$ groups at low temperatures. At temperatures $> 385^\circ\text{C}$ one methyl group is lost, at 500°C another methyl group. The oxygen atom of the second or third $\equiv\text{Si-O-Si}\equiv$ link formed subsequently may either come from a surface SiOH or from water which could still be present on the Cab-O-Sil.

To check this, the Cab-O-Sil was dried over P_2O_5 . After reaction with HMDS (sample nos. 25–28 in Table 1), ^{29}Si NMR spectra were recorded (Figure 3). (The reaction at 480°C was performed in a vitreous quartz ampoule in order to minimize the release of water by the reaction vessel). Now heating to at least 480°C is required in order to produce a signal of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups. At 500°C , the $-\text{OSi}(\text{CH}_3)_3$ signal has disappeared, and a weak signal of $(-\text{O})_3\text{SiCH}_3$ emerges.

In addition, some silylated Cab-O-Sil samples were reheated to higher temperatures. In such Cab-O-Sil samples water is probably absent. Thus, samples 7 and 26 were heated to 400°C and 500°C respectively (samples 21 and 23) (Figure 4). The spectra show very weak signals of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ and the signal of $(-\text{O})_3\text{SiOH}$ is still present.

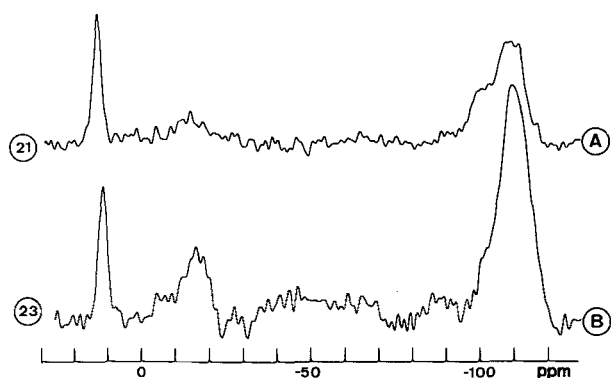


Figure 4

^{29}Si NMR spectra of Cab-O-Sil samples silylated with HMDS and reheated. A) silylated at 25°C, reheated to 400°C. B) dried over P_2O_5 , silylated at 460°C; reheated to 500°C. (The encircled numbers refer to the sample nos. in Table 1.)

From this we conclude that the absence of water in the sample impedes the formation of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups. Since the reagent HMDS is absent, the $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups, which are formed in small numbers, must originate from $-\text{OSi}(\text{CH}_3)_3$ groups that form a second $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ link.

3.3 Reaction with DPTMDS

Samples 13–17 (Table 1) were prepared with DPTMDS and ^{29}Si NMR spectra were recorded (Figure 5). Up to 200°C three signals are found: at +2 ppm of the $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ group and the usual signals in the -101 to -110 ppm range. Already at 300°C a signal at -16 ppm of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ appears and at 350°C the signal of $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ is lost. The dimethylphenylsilyl groups lose their phenyl rather than a methyl group and the resulting formation of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups occurs at considerably lower temperatures than in the reaction of Cab-O-Sil with HMDS.

The loss of the phenyl group was confirmed by ^{13}C CP-MAS-NMR of samples 13, 17, and 22. The spectrum of no. 17 showed no phenyl signal and no. 22 showed a reduction of this signal relative to the signal of the methyl groups. Also, the presence of benzene was established with GC-MS in the ampoule after reaction at 400°C.

The possible role of water in this process was studied again by reacting Cab-O-Sil dried over P_2O_5 with DPTMDS (samples 29–32 in Table 1). Now only above 400°C do other signals than that of $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ appear (Figure 6). Among these $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ is present at -16 ppm, but the other signals between +2 ppm and -16 ppm remain as yet unexplained. Judging from the ^{29}Si NMR chemical shifts alone an assignment to $-\text{OSi}(\text{CH}_3)(\text{C}_6\text{H}_5)_2$ would seem logical (replacing one methyl by one phenyl shifts the ^{29}Si

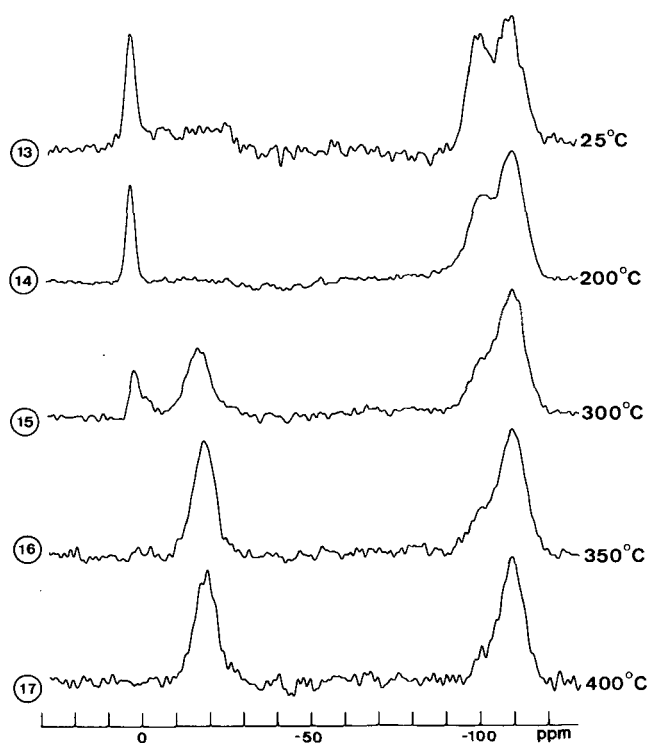


Figure 5

^{29}Si NMR spectra of Cab-O-Sil samples silylated with DPTMDS at the indicated temperatures. (The encircled numbers refer to the sample nos. in Table 1.)

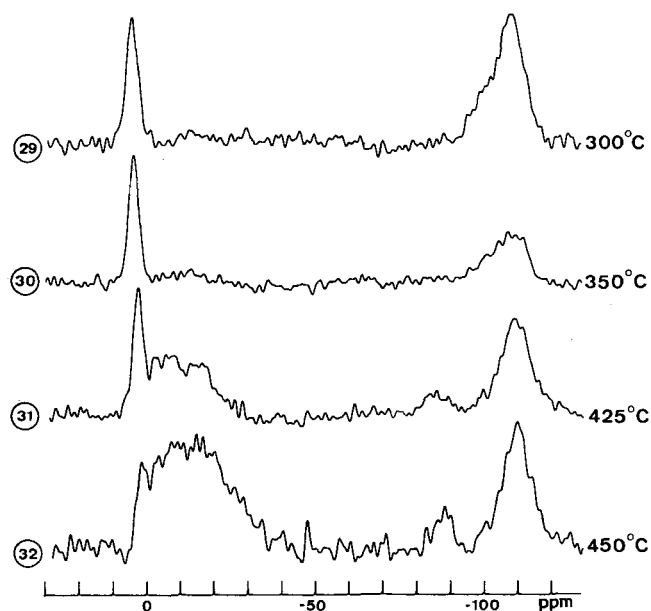


Figure 6

^{29}Si NMR spectra of Cab-O-Sil samples dried over P_2O_5 and silylated with DPTMDS at the indicated temperatures. (The encircled numbers refer to the sample nos. in Table 1.)

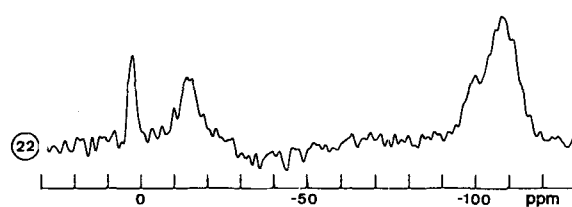


Figure 7

^{29}Si NMR spectrum of a Cab-O-Sil sample silylated at 25°C with DPTMDS and reheated to 400°C. (Sample no. 22 in Table 1.)

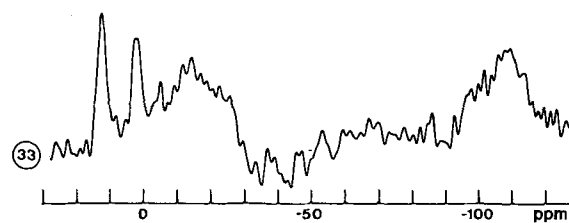


Figure 9

^{29}Si NMR spectrum of a Cab-O-Sil sample silylated with HMDS and DPTMDS (1:1 mol ratio) at 370°C for 72 hrs. (Sample no. 33 in Table 1.)

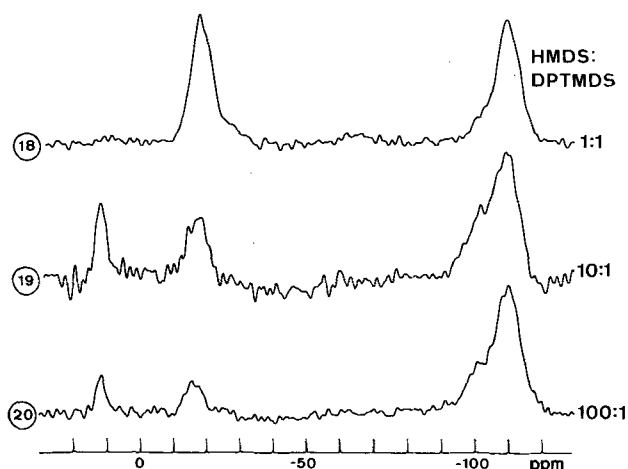


Figure 8

^{29}Si NMR spectra of Cab-O-Sil samples silylated at 400°C with different mixtures of HMDS and DPTMDS (mol ratios). (The encircled numbers refer to the sample nos. in Table 1.)

signal of silanes upfield by ca. 8–10 ppm). From a chemical point of view, however, such an assignment would not be compatible with previous conclusions.

An already modified Cab-O-Sil (sample no. 13) also was heated to 400°C (no. 22). The NMR spectrum (Figure 7) shows both $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ and $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ signals and the $(-\text{O})_3\text{SiOH}$ signal is reduced. Again we conclude that the absence of water in the sample impedes the formation of a second siloxane link, but the dimethylphenylsilyl group loses its phenyl group more readily than the trimethylsilyl group its methyl group.

3.4 Mixtures of HMDS and DPTMDS

Grob [3] introduced the use of mixtures of DPTMDS and HMDS. To study this, we silylated Cab-O-Sil at 400°C with different mixtures of HMDS and DPTMDS (samples nos. 18–20 in Table 1) and ^{29}Si NMR spectra were recorded

(Figure 8). The Cab-O-Sil silylated with a 1 : 1 (mol) mixture shows only a signal of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ and compared to the reaction with pure HMDS (sample no. 11, Figure 2), the signal of $-\text{OSi}(\text{CH}_3)_3$ is absent. This raised the question whether the DPTMDS acts as a catalyst or just reacts faster than HMDS with the Cab-O-Sil. In order to check this point reactions with 10:1 (mol) and 100:1 (mol) HMDS : DPTMDS were executed. Both samples show signals of $-\text{OSi}(\text{CH}_3)_3$ and $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups and resemble Cab-O-Sil that has reacted with pure HMDS (Figure 2, sample no. 11). In order to confirm this point further Cab-O-Sil was reacted with a 1 : 1 mixture at 300°C for 72 hours with only 2.5 $\mu\text{mol}/\text{m}^2$ (sample no. 33 in Table 1). The ^{29}Si NMR spectrum (Figure 9) now indeed shows signals of both $-\text{OSi}(\text{CH}_3)_3$ (+12 ppm) and $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ (+2 ppm) as well as a very weak signal of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ (-16 ppm).

From these results we conclude that in a mixture of HMDS and DPTMDS, the DPTMDS does not act as a catalyst, but only reacts more easily with the Cab-O-Sil.

4 Recapitulation of the NMR-Spectra

The NMR measurements have shown that the monofunctional reagents HMDS and DPTMDS yield only $-\text{OSi}(\text{CH}_3)_3$ and $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ surface groups, respectively, at low reaction temperatures (< 350°C and < 250°C respectively). At higher temperatures increasingly more $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups are formed. For DPTMDS this formation is complete at 350°C; for HMDS at 400°C $-\text{OSi}(\text{CH}_3)_3$ groups are still present and at 500°C there are still $(-\text{O})_3\text{Si}(\text{CH}_3)$ groups. In the case of DPTMDS the formation of these double siloxane links is accompanied by a loss of the phenyl group rather than of a methyl group: a signal of a $(-\text{O})_2\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)$ group was not observed (an estimated ^{29}Si NMR chemical shift for this group is $-16-(\text{ca. } 10) = -24/-26$ ppm). The second $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ link of a surface silyl group may either result from a reaction with a neighboring unreacted surface silanol group or with neigh-

boring attached silyl groups. In the latter case $\equiv\text{Si-O-Si}\equiv$ crosslinks are formed between the attached silyl groups. If the Cab-O-Sil is completely dry (kept over P_2O_5 for several weeks), the formation of these double $\equiv\text{Si-O-Si}\equiv$ links occurred for HMDS only at temperatures above 460°C and for DPTMDS only above 425°C . Therefore we conclude that water supplies the oxygen for these siloxane links, which consequently must be mainly crosslinks.

Taking into account the small size of the Cab-O-Sil M5 particles (8–10 nm) it seems likely that a number of $\equiv\text{Si-O-Si}\equiv$ links must bridge the gap between two particles. The distance between two particles, however, is too large for one $\equiv\text{Si-O-Si}\equiv$ unit.

Longer siloxane chains are necessary that can only be formed if sufficient water is present and at sufficiently high temperatures. Such chains may be formed in advance from the reagent and water by a gas phase reaction, or may be built up bit by bit from surface groups. Naturally, these chains may also be attached with both ends to the same particle.

Most spectra show that the formation of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ moieties is accompanied by a loss of $(-\text{O})_3\text{SiOH}$ groups. At this stage, it is still unclear in which way these two phenomena are related. The $-\text{OSi}(\text{CH}_3)_3$ groups (or $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ groups) already attached can react with an adjacent silanol group, or the reagent can react with the silanol groups by an, as yet, unknown mechanism, in which it loses a methyl (or phenyl, respectively) group. Further research on this topic is in progress.

The ^{29}Si NMR spectra of already silylated Cab-O-Sil heated to 400°C indicate that in the absence of additional reagent and water, the $-\text{OSi}(\text{CH}_3)_3$ or $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ groups already formed are only partially capable of further reaction.

5 Conclusions in Respect of Chromatography

Godefroot *et al.* [27] proposed a reaction mechanism in which, at temperatures of $300^\circ\text{--}400^\circ\text{C}$, the $-\text{OSi}(\text{CH}_3)_3$ groups initially formed leave the surface again by reaction with neighboring unreacted $(-\text{O})_3\text{SiOH}$ groups, yielding thus Si-O-Si bridges and $(\text{CH}_3)_3\text{SiOH}$. Our results indicate that the high temperatures used in the silylation of capillary columns are probably necessary to produce, starting from the monofunctional reagents HMDS and DPTMDS, dimethylsilyl surface groups with two siloxane links. The number of these groups depends on the amount of water and the reaction temperature. It might even be possible that short dimethylsiloxane chains are formed on the surface. Li Yu-Fu *et al.* [28] showed that there is, even in the reaction with D4, a strong preference for the formation of chains consisting of two dimethylsiloxane units. This leads

to a higher coverage and better shielding of the surface. Moreover, we found that concomitantly with the formation of $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups, the silanol groups disappear, which also reduces adsorption in chromatography.

We found that the water content of the sample considerably influenced the final result. This may explain the less successful silanization of fused silica capillaries because their water content is lower than that of glass capillaries. Usually, glass capillaries are heavily leached with hydrochloric acid in order to remove metal ions. This produces a so-called "hydro-gel" layer which must be dehydrated.

It is clear in the light of the results of the present study that the dehydration must be strictly controlled so as to leave a well defined amount of water on the surface. The sometimes erratic results of the silylation of leached and dehydrated glass columns may well originate from a careless and inadvertent dehydration procedure.

Deactivation with DPTMDS yields $-\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5$ groups only at low reaction temperatures. At higher temperatures $(-\text{O})_2\text{Si}(\text{CH}_3)_2$ groups are formed and the final result of a silylation with DPTMDS conducted at 400°C is the same as had HMDS been used. On the other hand, DPTMDS loses its phenyl group at a lower reaction temperature than HMDS loses a methyl group and one may regard this as a moderate advantage. Using a mixture of HMDS and DPTMDS in excess in the silylation of a column, the DPTMDS will react more readily than the HMDS with the surface, but again the final result is the same as had pure HMDS or DPTMDS been used.

The loss of the phenyl group in the reaction with DPTMDS also explains the almost unchanged wettability of a glass surface after silylation at 400°C with DPTMDS as compared to silylation with HMDS [5].

Whether an improved wettability can be expected by increasing the phenyl content or chain length in silylation agents, as suggested in some recent studies on column deactivation [29–32], is a subject of further research.

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