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Deactivation of Silica Surfaces with a Silanol-Terminated Polysiloxane; Structural Characterization by Inverse Gas Chromatography and Solid-State NMR

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Summary

Retention gaps deactivated with Silicone OV-1701-OH show good chromatographic performance and remarkable stability against water induced stationary phase degradation. In an attempt to better understand the fundamentals of the deactivation process using silanol terminated polysiloxanes, a fumed silica was deactivated with Silicone OV-1701-OH. In contrast to fused silica capillaries, fumed silica (Aerosil A-200) can be studied by ²⁹Si cross-polarization magic-angle-spinning (CP MAS) NMR, thus serving as a model substrate for fused silica. Retention data from inverse gas chromatography at infinite dilution and ²⁹Si CP MAS NMR data of five Aerosil phases, differing in residual silanol surface concentration, are correlated with the aim of validating this approach for stationary phase characterization. A comparatively detailed model of the deactivating polymer layer that explains the observed adsorption activities is deduced.

Surface silanols are shown to play a key role in the formation of the polymer layer, the structure of which is of primary importance for the adsorption behavior after deactivation. Contrary to common belief, the absolute silanol surface concentration after deactivation is only of secondary importance for the overall adsorption activity. High silanol surface concentrations enhance degradation of the polysiloxane chains into small cyclic fragments as well as subsequent adsorption and immobilization to the silica substrate surface. The mobility of linear polysiloxane chains in the kHz regime (as determined by NMR cross-polarization dynamics) appears to determine the extent to which the residual silanols are accessible for analytes. It is therefore anticipated that there is an optimum silanol surface concentration of fused silica surfaces to be deactivated with silanol terminated polysiloxanes: it should be large enough to adsorb polymer fragments, but not too large to avoid excessive residual silanol activity.

1 Introduction

Stationary phase stability is an important factor in a wide range of chromatographic techniques. More precisely, the lack of stability against aggressive sample components such as water can be a serious problem when using fused silica capillary retention gaps in the gas chromatographic analysis of (wet) samples.

Grob reported that a thin layer of the polar stationary phase OV-1701-OH on the fused silica capillary wall, when compared to other silylation procedures, provides increased inertness against water-induced degradation of precolumn performance [1]. However, as very often is the case in stationary phase development research, success was achieved by a trial and error

process. Experience gained in this way often lacks the theoretical background that could very well facilitate further progress in this field [2]. As a consequence, studies dealing with stationary phase development and chromatographic characterization are to a large extent based on concepts not always rigorously verified.

Precolumns (or retention gaps) are used in capillary GC to enable reconcentration of broadened solute bands after large volume injections of, for example, aqueous samples. In a series of papers, Grob outlined some of the difficulties encountered using this retention gap technique regarding the chromatographic characteristics of the precolumn. The ideal precolumn should be inert with a low retentive strength, wettable by the sample liquid, stable against water, and non-porous [3]. Unfortunately, neither water-wettable precolumns with sufficient inertness, nor inert precolumns that were water-wettable could be prepared [4]. This necessitated the use of appropriate solvent mixtures of water and an organic component [3]. Even in these cases, however, stability against water attack proved to be insufficient. Deactivations using OV-1701-OH appeared to be the best available, though still not good enough for use on a routine basis. Finally, the deactivation procedure was optimized by van der Hoff *et al.*, in collaboration with Grob [3]. The latter work is the basis from which we started our experiments.

OV-1701-OH is a silanol-terminated, relatively polar polydimethylsiloxane with 7% cyanopropyl and 5% phenyl substitution. Madani *et al.* were the first to recognize the unique characteristics of an end-chain silanol functionality [6]. In the deactivation of borosilicate tubes with a silanol-terminated polydimethylsiloxane they suggested that the end groups participate in the chemical bonding to the glass surface. Verzele *et al.* extended this approach when they coated fused silica capillaries with silanol-terminated methylphenylsiloxane polymers [7]. Yet, they did not mention the possible role of terminal silanols in surface bonding reactions. Lipsky and McMurray claimed to have evidence for the formation of a covalent linkage between silanol-terminated non-polar siloxanes and the underlying fused silica surface [8]. However, they appear convinced that terminating silanol functionalities of polar polysiloxanes do not chemically interact with surface silanol groups. Blum, shortly thereafter, stated that for medium polar silanol-terminated siloxanes the coating is essentially based on condensation processes between silanol groups of the phase and (residual) silanols of the support surface [9]. The latter opinion has become widely ac-

cepted. However, Blum very unfortunately stated that no extension to apolar phases had been attempted at that time. Among other things, this remark initiated a lively discussion between Lipsky and Blum [10]. Irrespective of the exact chemical background of the coating procedure, all authors agree on the advantageous properties of silanol-terminated polysiloxanes as coating materials. These are improved wettability of the fused silica capillary wall during initial coating [6,9], improved thermal stability [2,6,11], high inertness and efficiency [2,9], and the ease of production by performing deactivation and immobilization in a single step [7–9,12].

In the present contribution, attention is focused on a more fundamental characterization of the structure of the OV-1701-OH phase. The ultimate goal is to provide the chemical background for the favorable properties of OV-1701-OH coated vitreous silica by describing the stationary phase structure as detailed as possible. Our earlier work has shown how inverse gas chromatography (IGC) and solid-state nuclear magnetic resonance can be used to investigate the adsorption characteristics of trimethylsilylated Aerosil [13], a vitreous silica introduced as a model substrate for fused silica in ^{29}Si NMR analysis by Rutten *et al.* [14]. The results of that work encouraged us to further investigate the merits of this approach on practical issues encountered in modern gas chromatography. The results of Van der Hoff *et al.* [3] in obtaining maximum stability against water-induced phase degradation by empirically optimizing the coating procedure with OV-1701-OH, seemed a good starting point in order to evaluate the approach combining IGC and ^{29}Si CP MAS NMR. Thus, the present work focuses on how IGC and solid-state NMR are used to characterize freshly OV-1701-OH coated Aerosil particles. This approach enabled us to propose a detailed structural model for this polymer-coated silica system.

2 Experimental

2.1 Materials

Aerosil A-200 (Degussa AG, Frankfurt, Germany), a non-porous vitreous silica with an average particle diameter of 12 nm and a specific surface area of 200 m²/g, was used as a model substrate for fused silica. Silicon OV-1701-OH was purchased from Fluka Chemie AG (supplied by Omnilabo, Breda, The Netherlands). It is a silanol-terminated polydimethylsiloxane with 5% phenylmethyl substitution and 7% cyanopropylmethyl substitution respectively. According to the supplier, the silanol content is approximately 12%. This was verified by ^{29}Si High-Resolution NMR spectroscopy. Probe solutes for the IGC-experiments were purchased from different suppliers and used as received [13].

2.2 Silica Pretreatment

The Aerosil particles were de- and rehydrated as described earlier [13]. This starting material will be referred to as A0. To study the influence of the silanol surface concentration on the deactivation result, four batches of the A0 material were (partly) dehydrated again by high temperature treatment for 24 hours at respectively 200, 350, 500, and 700 °C in an ambient atmosphere. The resulting four pretreated batches will be referred to as A1, A2, A3, and A4. Before the deactivation procedure, each of the five Aerosil batches was analyzed by ^{29}Si cross-polarization magic-angle-spinning (CP MAS) NMR, after drying at 110 °C in vacuum (10^{-2} Torr) for 6 hours.

2.3 Deactivation Procedure

In a typical deactivation experiment, 500 mg of dry Aerosil was placed in an 8 mm inner diameter quartz ampoule, which was then evacuated and filled with dry argon gas (99.997%, Hoek Loos, Schiedam, The Netherlands) after which 2.5 ml of a 5% (w/w) OV-1701-OH solution in hexane (distilled prior to use) was added. This amount of siloxane polymer would result in a final film thickness of approximately 1 nm, generally accepted as enough to shield underlying surfaces [5,15]. The Aerosil was suspended by vigorously shaking the mixture and by a short (5 s) ultrasonic treatment. Flocculation by polymer chains bridging the Aerosil particles was not observed. The suspension was degassed by several freeze-thaw cycles, after which the hexane was slowly evaporated at room temperature under reduced pressure. The coated Aerosil was further dried under vacuum for 30 minutes. After flame-sealing the quartz ampoule, it was placed in a GC oven (Perkin Elmer 8500 GC, Beaconsfield, England) and the same temperature program was used for deactivation as in reference 5: from 50 to 300 °C with 4°/min, 1 hour isothermal at 300 °C. Finally, the ampoule was opened and the deactivated Aerosil powder was stored over P₂O₅ before IGC and NMR analysis. These polymer-coated phases will be referred to as P0, P1, P2, P3, and P4 respectively (the Arabic numerals referring to the pretreated substrates A0, A1, A2, A3, and A4).

2.4 NMR Measurements

NMR spectra were collected on a Bruker MSL-400 NMR spectrometer (Bruker Analytik GmbH, Rheinstetten, Germany) at 79.4 MHz. To estimate the number-average chain length of the OV-1701-OH polymer, a single pulse, proton-decoupled ^{29}Si High-Resolution NMR spectrum of a 10% (w/w) solution in deuterated dichloromethane (approximately 0.1 M in chromium acetylacetonate as relaxation agent) was recorded with pulse interval times of 60 s. The ratio of end group signals ($\delta = -11$ ppm relative to tetramethylsilane (TMS)) and siloxane chain signals ($\delta = -19$ to -22 and -37 to -39 ppm) then is a reliable measure of the average degree of polymerization [16].

Solid-state ^{29}Si CP MAS NMR spectra of the pretreated Aerosils and the polymer-coated phases were collected using high-power proton decoupling ($\omega_{\text{1H}} = 35$ kHz) at a MAS frequency of 2500 Hz, using 7 mm double bearing rotors filled with typically 200 mg of siliceous material. The Hartmann-Hahn match for effective cross-polarization was checked with Q₈M₈ (the trimethylsilyl ester of cubic octameric silicate) which also served as an external chemical shift reference. 1600 Free induction decays were co-added per spectrum in 1K data points. No additional line broadening was applied before Fourier transformation. Each spectrum was deconvoluted using the Bruker Winfit program. Contact time variation was employed and deconvoluted signal intensities or areas were plotted as a function of contact time in cross-polarization (CP) curves. The relaxation parameters T_{HSi} (the proton-silicon cross-polarization time) and $T_{1\rho\text{H}}$ (the proton rotating frame relaxation time) and the maximum obtainable magnetization M_0 (a measure of the absolute number of proton bearing surface moieties) were estimated for the different signals by fitting the CP-curves to eq. (1) [17], using a least-squares iterative program. In this equation, M_t is the observed magnetization in intensity or area units at contact time τ . The M_0 values determined for the deconvoluted signal areas were corrected for variations

$$M_{\tau} = \frac{M_0}{T_{\text{HSi}}} \times \frac{e^{-\tau/T_{1\rho\text{H}}} - e^{-\tau/T_{\text{HSi}}}}{1/T_{\text{HSi}} - 1/T_{1\rho\text{H}}} \quad (1)$$

in silica sample weight and spectrometer performance. The parameters T_{HSi} and $T_{1\rho\text{H}}$ are the time constants for describing the cross-polarization dynamics of the surface structures. They are related to the mobility of the protons involved in cross-polarization to the specific silicon nucleus. Mobility in this respect is defined as a fluctuation in the position of the proton with respect to the position of the chemically bonded silicon atom. Large T_{HSi} values indicate mobility of the ^1H - ^{29}Si internuclear vector in the 10^2 - 10^3 Hz range, large $T_{1\rho\text{H}}$ values are indicative of mobility in the proton reservoir in the 10^4 - 10^5 Hz range.

2.5 IGC Experiments

The procedure for the inverse gas chromatographic experiments at infinite dilution was as described earlier [13]. A constant inlet pressure of 4.0 bar was applied. Dead time delays were calculated using the best regression line through the linear relation between $\ln(t_r - t_0)$ and the homologue numbers of the *n*-alkanes pentane up to and including undecane.

3 Results and Discussion

3.1 NMR experiments

In order to estimate the silanol surface concentration of the five Aerosil substrates A0–A4, the CP-curves of the deconvoluted Gaussian signal areas of Q^2 (disilanol, ^{29}Si NMR signal at -90 ppm) and Q^3 (single silanol, ^{29}Si NMR signal at -100 ppm) were fitted to eq. (1) to give the parameter M_0 . As the fully hydrated fumed silica has a silanol surface concentration of $8.45 \mu\text{mole}/\text{m}^2$ [18], the sum $M_0(\text{Q}^3) + 2M_0(\text{Q}^2)$ of the substrate A0 is used as a reference value. Dividing this sum for the other substrates by the reference value of A0 gives an estimate of the silanol surface concentration as a function of pretreatment temperature. The results are listed in **Table 1**. The calculated values are in good agreement with literature data on thermally dehydrated amorphous silicas [19]. In **Figure 1**, the spectra of the different substrates obtained at a contact time of 10 ms are shown. The decrease in Q^2 and Q^3 signal intensities nicely displays the decrease in silanol surface concentration with increasing pretreatment temperature. Of course also the signal of surface siloxanes (Q^4 , -110 ppm) decreases as the source of proton-silicon cross-polarization becomes smaller. The silicon nuclei in these groups can only be cross-polarized by more distant protons on neighboring Q^2 and Q^3 sites.

Table 1. Pretreatment temperature and resulting silanol surface concentrations, Γ_{SiOH} , of the Aerosil substrates A0–A4 as determined by ^{29}Si CP MAS NMR.

Aerosil substrate	Pretreatment temperature [°C]	Γ_{SiOH} [$\mu\text{mole}/\text{m}^2$] ^{a)}
A0	110	8.45
A1	200	5.3
A2	350	3.5
A3	500	2.9
A4	700	2.2

^{a)} Estimated errors: $0.2 \mu\text{mole}/\text{m}^2$.

Figure 1. ^{29}Si CP MAS NMR spectra of the pretreated Aerosils A0–A4. Contact time = 10 ms.

Figure 2. ^{29}Si High Resolution NMR spectrum of a 10% (w/w) solution of OV-1701-OH in CD_2Cl_2 (0.1 M chromium *tris*-acetylacetonate). The polymer terminal Si-OH signal is shown in the insert. Number of scans = 1144.

Figure 2 displays the single-pulse, ^{29}Si High-Resolution NMR spectrum of the OV-1701-OH polymer solution in CD_2Cl_2 . The observable splittings of the NMR signals are a result of the neighboring group effect [20,21]: the chemical shift of a certain silicon nucleus in the polymer chain is dependent on the type of the neighboring siloxane group (dimethyl, cyanopropylmethyl, phenylmethyl or a silanol end group). The signal area ratio of end- to chain-groups is 1:130, resulting in a number-average chain length of approximately 260 siloxane units. From the 7% cyanopropyl and 5% phenyl substitution, a number average molecular weight of 17,400 g/mole can be calculated. This implies that in the deactivation procedure, about $0.2 \mu\text{mole}$ silanols per square meter substrate are introduced. This value is of importance when discussing the number of substrate silanols disappearing after deactivation (*vide infra*).

In **Figure 3**, ^{29}Si CP MAS NMR spectra of the phases P0–P4 obtained with a contact time of 10 ms are depicted. Signal assignments are based on literature data [22]. The chemical shift region from about 0 to –40 ppm contains signals that result from (degradation products of) the OV-1701-OH material. From right to left, there is a resonance at –37 ppm, assigned to methylphenylsiloxane units, and a sharp line at –22 ppm due to dimethylsiloxane units. The latter signal is flanked at the low field side by a shoulder slowly losing intensity in the low field direction. This shoulder indicates the presence of polymer degradation products: siloxane ring structures (particularly trisiloxanes and larger), but also the methylcyanopropylsiloxane signal is expected in this region. For deconvolution of this rather complicated signal (from 0 to –25 ppm) a total of four Gaussian curves was chosen, as this appeared to be the minimum number of components to obtain a satisfactory fit to the experimental ^{29}Si CP MAS NMR signal.

Figure 3. ^{29}Si CP MAS NMR spectra of the phases P0–P4. Contact time = 10 ms. For signal assignments see text.

Table 2. ^{29}Si CP MAS NMR relaxation parameters ^{a)} of the surface silanols and polymer dimethylsiloxane groups on the phases P0 to P5, and the residual silanol surface concentrations ^{b)} after deactivation (and the change therein with respect to the pretreated substrate ($\Delta\Gamma_{\text{SiOH}}$)).

Phase	Q ³ silanols		Polymer chain	Γ_{SiOH} [$\mu\text{mole}/\text{m}^2$]	$\Delta\Gamma_{\text{SiOH}}$
	T_{HSi}	T_{IPH}	T_{IPH}		
P0	0.98	37	65	5.6	–2.8
P1	1.0	49	150	4.1	–1.2
P2	1.2	93	361	3.3	–0.3
P3	1.3	310	206	2.5	–0.4
P4	2.2	513	68	2.5	+0.3

^{a)} Estimated error: $\pm 10\%$.

^{b)} Estimated error: $\pm 0.2 \mu\text{mole}/\text{m}^2$.

The relaxation parameters from the CP-curve analyses of the Q³ signals and the most intense OV-1701-OH signal at –22 ppm are summarized in **Table 2**. For the Q³ signals also the calculated silanol surface concentrations of the phases are listed, together with the change with respect to the starting Aerosil substrate.

3.2 IGC Experiments

The change in free energy of adsorption per methylene group of the *n*-alkanes ($\Delta(\Delta G_{\text{CH}_2})$) and the specific free energy of adsorption (ΔG_{spec}) to the Aerosil/OV-1701-OH surface of six probe solutes with different chemical functionalities were measured as described in reference 13. Whereas ($\Delta(\Delta G_{\text{CH}_2})$) was not significantly different for the phases P0 to P4 ($1.8 \pm 0.1 \text{ kJ/mole}$), **Figure 4** shows that the free specific energy of adsorption differs considerably between phases when plotted as a function of the pretreatment temperature of the Aerosil silica before deactivation. The maximum errors in ΔG_{spec} were determined to be 0.2 kJ/mole. From this picture it is clear that all solutes are most strongly retained on the phases P1 and P2, while P4 exhibits the weakest adsorption strength. In comparison to the data in our earlier publication [13], which were measured on trimethylsilylated Aerosil surfaces, the present values are considerably smaller (by about 9 to 10 kJ/mole for the hydrogen-bonding solutes propanenitrile, dipropylether and 3-pentanone, and about 2 to 3 kJ/mole for the non-hydrogen-bonding solutes 1-heptene, 1-chloropentane, and toluene). Thus, taking the specific adsorption energy as a criterion, the OV-1701-OH treatment is far superior to trimethylsilylation with respect to deactivation of adsorptive surface sites.

Figure 4. Free specific energies of adsorption, ΔG_{spec} of the probe solutes to the phases P0 to P4, represented as a function of the pretreatment temperature of the Aerosil substrate.

3.3 Discussion

In the literature there is consensus of opinion that before deactivation there should be an optimum ratio of substrate surface silanols to polymer end-group silanols, in order to produce a stable, sufficiently inert chromatographic stationary phase [3,8,9]. Generally it is assumed that the more silanols remain in the prepared stationary phase, the more adsorptive it will be. However, when the specific adsorption energy of, for example,

Figure 5. Specific free energies of adsorption, ΔG_{spec} , of propanenitrile to the phases P0 to P4 as a function of the surface silanol concentration after deactivation with OV-1701-OH.

propanenitrile (a compound capable of forming hydrogen bonds to silanols), is plotted as a function of silanol surface concentration on the deactivated phases (Figure 5), there turns out to be no such straightforward relationship. In fact all probe solutes exhibit specific free energies of adsorption on the phases P1 and P2 that are comparable to, or even higher than those on the phase P0. Note that P0 has a significantly higher silanol surface concentration. Also remarkable is the adsorptive difference between the phases P3 and P4, which have about the same silanol surface concentration. The specific free energy of adsorption of propanenitrile is roughly 60 % lower on the phase P4 than on P3.

The former observations imply that the residual silanols on the different phases are not alike and that there must be an important difference between the silanols on for example P3 and P4. The ^{29}Si CP MAS NMR relaxation parameters in Table 2 reveal that the silanols on P4 have a larger mobility, indicated by significantly larger T_{HSi} and $T_{1\rho\text{H}}$ values (see also the Experimental Section 2.4). Chuang *et al.* [23] demonstrated that silanols experiencing maximal steric shielding have very long relaxation times (T_{HSi} and $T_{1\rho\text{H}}$); there is no particular favored directional orientation and consequently the Si-O-H internuclear vector is dangling 'freely' around the Si-O bond axis. As the relaxation parameters of the surface silanols in our case resemble those of the internal silanols as described by Chuang *et al.*, the surface silanols on P4 appear to be much better sterically shielded than on P3. There even is a trend in the T_{HSi} and $T_{1\rho\text{H}}$ values, going from P0 to P4. This is clearly illustrated in Figure 6 where the CP-curves of the Q^3 signals of the phases P0–P4 are plotted. When the number of silanols on the pretreated substrate is lower, they exhibit an increased mobility of the ^1H - ^{29}Si internuclear vector after OV-1701-OH deactivation.

Interesting to note is that on P4 the silanol surface concentration actually increased during deactivation, roughly by the amount of silanols present in the OV-1701-OH itself (*vide supra*). This can be understood when considering the possible modes of surface attachment of the polymer chains during high temperature deactivation as represented in Figure 7. First, the decrease in silanol surface concentration when deactivating the substrates A0 to A3 is caused by the condensation of polymer silanol end-groups and

Figure 6. Cross-polarization curves of the ^{29}Si NMR signal of single silanols (Q^3 , ~ 100 ppm) of the phases P0 to P4. Note the decrease in maximum intensity and the increase in $T_{1\rho\text{H}}$ (illustrated by flattening of the CP-curve at longer contact times) when going from P0 to P4.

Figure 7. Reaction pathways for the attachment of OV-1701-OH to the Aerosil substrate surface.

substrate silanols (reaction 1). Second, degradation of attached polymer chains results in new polymer silanol end-groups (reaction 2), which in turn can be bonded to the substrate surface through reaction 1. The net effect of chain degradation thus also is a decrease in silanol surface concentration. The absence of a significant ^{29}Si NMR signal of polymer silanol end-groups (to be expected at ~ 11 ppm) in the spectra of P0 to P2 (Figure 4) indicates that the vast majority of polymer silanols, formed during degradation, find a second silanol for undergoing a condensation reaction. The attack of a strained substrate siloxane bridge by a polymer silanol end group (when substrate silanols are only scarcely available like on the A4 surface) results in an increase

of the overall surface silanol concentration. Reaction 3 in Figure 7 then explains the increase in silanol surface concentration observed for P4 with respect to A4. Finally, in reaction 4 the attack of the polymer siloxane backbone by strained silica siloxane bridges is displayed. At higher dehydroxylation temperatures ($> 200\text{ }^{\circ}\text{C}$) strained siloxane bridges (surface defects) are formed on the silica surface [24,27]. The reactivity of these particular siloxane bonds should not be underestimated, since they have been shown to be the cause of methanol decomposition on temperature activated silica surfaces [27]. Moreover, Blümel [28] stated that the silylation of dehydrated silica with ethoxysilanes occurs directly through reaction with strained siloxane bonds that are even more reactive than isolated silanol groups. Thus, also the attachment of the polymer siloxane chain to the temperature treated Aerosil silica substrate by reaction 4 is feasible.

The concentration and degree of steric shielding of the silanol groups are not the only factors determining the final adsorptivity. This is evident when comparing the phases P0, P1, and P2. Although the silanol mobilities on these phases do not differ very much, P0 exhibits lower ΔG_{spec} values for all probe solutes than P1 or P2, even though P0 has the highest silanol surface concentration. Thus at least one other factor also controls the silanol adsorption activity. Careful consideration of the degree of chain degradation, to be observed in the spectra in Figure 3, reveals that P1 is the phase with the highest content of cyclic siloxane structures. The shoulder to the main -22 ppm dimethylsiloxane peak is larger than for any of the other phases (differences in CP dynamics taken into account). In Figure 8 a typical example of the deconvolution of the polymer siloxane signal region is presented. It is known from the literature that smaller cyclic siloxane structures have a larger chemical shift compared to linear structures because of the strained siloxane bridges [22]. Thus, the Gaussians 3, 2, and 1 (in that order) can be assumed to roughly represent cyclic polymer fragments with decreasing ring size. It is interesting to learn that the peak heights of the components 1, 2, and 3 exhibit the same cross-polarization dynamics on all five different phases. As summarized in Table 3, on all phases the T_{HSi} and $T_{1\rho\text{H}}$ values increase in the order of Gaussian no. 1 $<$ no. 2 $<$ no. 3. Therefore, ring size (ring rigidity) is the primary factor determining T_{HSi} and $T_{1\rho\text{H}}$ values. The cross-polarization dynamics of the fourth Gaussian component, however, vary considerably among the phases. Its CP behavior is nearly identical to the maximum of the total -22 ppm signal, data of which were already given in Table 2.

Now, the $T_{1\rho\text{H}}$ values of the intact linear chains, represented by Gaussian no. 4, show a large increase from P0 to P2 (see also Table 2). This means that on the phase P2, the one with the longest $T_{1\rho\text{H}}$, the siloxane chains have considerable motional freedom, whereas on phase P0 they are more rigid. The flexible chains on P2 could thus well be the cause of its high adsorption activity, as they facilitate access of solute molecules to the underlying silica substrate.

Taking all of the above arguments into consideration, we propose the following model for the formation of OV-1701-OH layers on vitreous silica surfaces. High initial silanol surface concentrations enhance degradation of the polymer chains at the deactivation temperature of $300\text{ }^{\circ}\text{C}$. The SiOH end groups of the polysiloxane chain react with silanol surface groups with the loss of water, after which degradation of the bonded chains and sub-

Figure 8. Typical example of the result of the deconvolution of the OV-1701-OH ^{29}Si CP MAS NMR signal using four Gaussian functions (nos. 1, 2, 3, and 4 as indicated).

Table 3. Cross-polarization parameters of the Gaussian components 1, 2, 3, and 4 of the deconvoluted OV-1701-OH ^{29}Si CP MAS NMR signal.

Gaussian no.:	T_{HSi}				$T_{1\rho\text{H}}$			
	1	2	3	4	1	2	3	4
P0	0.9	1.2	2.7	3.6	15	25	41	102
P1	0.9	1.3	2.9	4.4	16	28	62	297
P2	0.9	1.1	2.9	4.0	14	33	59	∞
P3	1.1	1.3	2.4	3.2	22	37	71	∞
P4	0.4 ^{a)}	1.0	2.1	4.0	10 ^{a)}	32	47	88

^{a)} Unreliable value due to a small signal to noise ratio in the NMR spectra.

sequent attachment of the chain fragments further consume surface silanols. This explains the decrease in silanol surface concentrations of the phases P0–P3 with respect to A0–A3. The smaller the remaining silanol concentration, the more mobile the chain segments on the silica surface are, illustrated by the large $T_{1\rho\text{H}}$ values of P2. Probably the higher concentration of residual silanols on P0 causes stronger adsorption of the covering polymer chains (for example through hydrogen-bonding with the cyano-propyl groups of OV-1701-OH [29].) As the silanols are then not available for solute interaction, P0 expresses slightly smaller specific adsorption energies towards the probe solutes than P1 and P2. The more mobile siloxane chains on P2 probably facilitate access to the underlying silica surface.

If the silanol surface concentration before deactivation is below a certain value (approximately $3\text{ }\mu\text{mole/m}^2$) chain degradation occurs much less. Also, it is anticipated that at low silanol surface concentrations the SiOH end-groups of the polymer attack strained siloxane bridges on the silica surface. Thus, surface silanols are actually formed during deactivation, as observed for P4. The covalently attached long polymer chains have a relatively rigid structure as indicated by the small $T_{1\rho\text{H}}$ values of the polymer siloxane units. This rigidity and the resulting shielding of remaining active surface sites may be induced by adsorption on residual silanols, more likely, however, by interchain interactions. Figure 9 very schematically sketches the proposed structure of the deactivating OV-1701-OH layer on the phases P0, P2, and P4.

Now, the chromatographically most useful deactivation procedure may well be one in which the silanol surface concentration of the fused silica capillary wall before deactivation is just large

Figure 9. Schematic representation of the structural characteristics of the OV-1701-OH layer on the silica surface of the phases P0, P2 and P4. P0: extensive degradation and adsorption of polymer fragments, P2: extensive degradation without subsequent adsorption, P4: minor degradation and stronger interchain interactions.

enough to allow the remaining silanols after deactivation to adsorb (immobilize) the polymer structures, but not too large as this would result in excessive degradation of the polymer chains during baking. Moreover, too high residual silanol surface concentrations will increase the affinity for water of the deactivating layer, which might enhance water-induced degradation of the deactivating layer. Translation of the results of the study of Van der Hoff *et al.* [3] in terms of the present work thus indicates that they probably have found an optimum silanol surface concentration by optimizing the intensity of leaching.

4 Conclusions

It is demonstrated that, when correlating IGC and NMR data of OV-1701-OH deactivated Aerosil, a fairly detailed model of the structural characteristics of the deactivation layer can be developed.

Contrary to common belief, the concentration of surface silanols is not directly related to adsorption activity of the silica surface after deactivation. This study provides good reason to believe that the silanol concentration primarily determines the structure of the OV-1701-OH layer. If the silanol surface concentration on the silica substrate is high, the polymer chains are degraded during deactivation and the remaining chain fragments are subsequently adsorbed. However, at intermediate silanol surface concentrations the polymer fragments exhibit large mobilities in the 10^4 to 10^5 Hz motional regime, which is assumed to facilitate access of solute molecules to the substrate surface and cause higher adsorption activity. On substrates with low initial silanol surface concentrations, chain degradation is of minor importance and the polymer chains adapt an ordered structure, probably through interchain interactions and adsorption by residual silanols.

Van der Hoff *et al.* [3] state that leaching as a pretreatment of fused silica capillaries is easily overdone when using OV-1701-OH as deactivation reagent. Therefore, we surmise that the structure of the deactivating layer on the Aerosil phase A4 resembles

that of the OV-1701-OH layer in their well deactivated fused silica capillary columns. When leaching is indeed overdone, the OV-1701-OH structure will be more like that of the Aerosil phases P3 and P2, resulting in capillaries with higher adsorption activities and inferior stability against water induced degradation.

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