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# Characterization of silica-based octyl phases of different bonding density

## Part I. Thermal stability studies

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### Abstract

Chemically bonded phases for reversed-phase chromatography are often produced via reaction of silica gel with appropriate organosilane. Although this reaction is commonly used and well-documented in literature, little attention has been paid so far to study the postreaction curing process. In the current paper the effect of the curing process on the thermal stability of the synthesized octyl phases has been investigated by means of thermogravimetry and solid-state NMR techniques. The study shows that the postreaction isothermal equilibration of the samples dramatically improves their thermal stability without a substantial mass loss due to thermodesorption of silane. Curing process promotes condensation reaction of surface hydroxyls with hydrolyzed silane molecules increasing surface coverage of the synthesized chemically bonded phases. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Silica; Stationary phases, LC; Octyl stationary phases; Thermal stability

### 1. Introduction

Chemically modified silica gels, also known as chemically-bonded phases, are widely used as packings in the reversed-phase liquid chromatography [1–5]. Although there is a variety of the specialty phases, meticulously designed for specific separation problems, a significant share of the reversed-phase columns available on market is represented by alkyl-phase columns ( $C_6$ ,  $C_8$ ,  $C_{12}$ ,  $C_{18}$ ) [2–4]. In fact, for many reversed-phase liquid chromatography separations the specialty phases are unnecessary, because a sufficient change of the separation selectivity can be achieved on the alkyl-phases by varying the mobile phase composition [3].

Typically, silica-based alkyl phases are synthe-

ized via reaction of silica gel with appropriate organosilanes [3–5]. The reaction can be conducted either in the gas phase or in the organic solvent (toluene, xylene) [4,5]. However, for long chain organosilanes the reaction in the gas phase is less favorable, because of the low vapor pressure of the corresponding organosilanes and subsequently arising problem of their thermal stability at high temperatures ( $>300^\circ\text{C}$ ). The reaction in the solution can be carried out with mono-, di-, and trifunctional organosilanes, which lead to formation of monomeric, oligomeric and polymeric chemically-bonded phases, respectively. Many of commercially available packings are produced via reaction with monofunctional organosilanes due to a greater batch-to-batch reproducibility of this process [3]. In the case of polyfunctional silanes even small differences in the amount of water present in the reagents or on the silica surface can cause significant variations of the

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amount of organic phase chemically attached to the surface [3,6,7].

Often, after completion of the silica gel-organosilane reaction an additional postreaction (e.g. curing) step is introduced. The curing step is done by heating the dried sample in the temperature range between 100 and 200°C. This step is designed to improve the stability and produce more densely packed film of the bonded phase. Despite the fact that the reaction of silica with organosilanes is well documented in literature [4,5,8,9], little attention has been paid so far to the curing process.

In earlier studies Macial [10] and Vansant [11], who investigated the effect of curing after derivatization of silica gel with trifunctional silanes, concluded that the curing process increases number of the Si–O–Si bonds. The increase could be attributed either to surface Si–O–Si<sub>s</sub> or intermolecular Si–O–Si bond formation. Recently a detailed study of the derivatization of silica with organosilanes was undertaken by Tripp and Hair [12], who investigated the hydrolysis of trichloro-, dichloro-, and monochloromethylsilanes on hydrated silica surface and the effects of curing in postreaction treatment of chemically modified silicas. Based on IR experiments it was shown that: (1) at the gas–solid interface methylchlorosilanes are fully hydrolyzed to methylsilanols due to the surface water of the hydrated silica; (2) the percentage of the adsorbed methylsilanols condensing with the surface hydroxyl groups follows the order (CH<sub>3</sub>)<sub>3</sub>SiOH > (CH<sub>3</sub>)<sub>2</sub>Si(OH)<sub>2</sub> > CH<sub>3</sub>Si(OH)<sub>3</sub>; (3) for trihydroxy- and dihydroxydimethylsilanols the curing process mostly completes cross-linking, and also results in a few attachments to the surface through Si–O–Si<sub>s</sub> bonds. In the case of trimethylsilanol lateral polymerization is not possible, and the curing process mostly results in removal of physically adsorbed silanol species from the silica surface.

In this work modification of silica was done with chromatographically relevant (i.e. octyl ligand) monofunctional organosilane and thermogravimetric technique was employed to obtain information on the stability of the freshly synthesized chemically-bonded phases and to provide important insights into the curing mechanism of the derivatized silica. Additionally, solid-state NMR technique was employed to monitor the formation of the Si–O–Si<sub>s</sub> bonds between silica surface and organosilyl group.

Finally, it should be mentioned that the current paper (Part I) should be viewed in a context of a consecutive project (Part II) focused on the evaluation of chromatographic properties of the synthesized silica-based octyl phases of different bonding density.

## 2. Experimental

### 2.1. Materials

Chromatographic silica gel Luna (batch 35 119) was donated by Phenomenex (Torrance, CA, USA). According to manufacturer's information, it has an average pore diameter of 10 nm, and particle size of 5 μm. The silanizing agent, *n*-octyldimethylchlorosilane, was obtained from Huls (Piscataway, NJ, USA). The reaction solvent, toluene of ACS grade, was purchased from Fisher (Pittsburgh, PA, USA). All reagents were used as received.

### 2.2. Synthesis of C<sub>8</sub> bonded phases

In order to activate silica surface before modification, a mixture of approximately 5 g of silica in 100 ml of water was vigorously stirred, and then sonicated for 2 min. After at least 3 h allowing the suspended silica to settle down at the bottom of the beaker, the water was carefully decanted, and wet silica was placed in an oven at 393 K for 22 h.

The activated silica gel was cooled to ambient temperature, and then placed in the reaction flask containing 150 ml of toluene. The mixture was softly stirred by bubbling dry nitrogen through the reactor. After equilibrating the system for 20 min the silanizing agent (*n*-octyldimethylchlorosilane) was added. In the synthesis of Luna-3.32 and Luna-1.60 octyl phases a five time excess of *n*-octyldimethylchlorosilane was used as compared to the amount required for complete reaction with surface hydroxyls assuming their maximum concentration of 8 μmol/m<sup>2</sup> [13]. Additionally, in the synthesis of Luna-3.32 phase 1 ml of pyridine as an acid scavenger was added to reaction mixture to promote higher coverage [4]. For Luna-1.20 phase only 1.2 time excess of *n*-octyldimethylchlorosilane was used.

Following an addition of the silanizing agent, the reactor temperature was brought up to approximately 122°C, i.e. when the reaction mixture started to boil

gently. After refluxing the mixture for 22 h the reaction was stopped, and the modified silica gel was cooled down to room temperature, transferred into a vacuum glass filter, and washed with toluene, acetone, acetonitrile, methanol and deionized water.

### 2.3. Thermogravimetry

In order to evaluate surface properties and thermal stability of the original and modified silica gels thermogravimetric analysis (TGA) was performed. All measurements were carried out in a flow of nitrogen under quasi-isothermal conditions using a model TGA 2950, high-resolution thermogravimetric analyzer from TA Instruments (New Castle, DE, USA). In each measurement approximately 20 mg of the silica sample was placed in an open platinum pan, and heated up to 1000°C at a heating rate of 5°C/min. In supplementary TG experiments the procedure was modified. An additional isothermal equilibration step in the temperature range between 140 or 250°C was added to the analysis method.

### 2.4. Solid-state NMR experiments

The variable contact time  $^1\text{H}$ - $^{29}\text{Si}$ -cross polarization (CP) magic angle spinning (MAS)-NMR experiments were performed on a Bruker DMX 400WB spectrometer (USA Bruker Instruments, San Jose, CA, USA) with  $^{29}\text{Si}$  Larmor precession frequency of 79.5 MHz. The samples were packed in 9 mm zirconia rotor and spun at MAS frequency of 2000 Hz using dry air driving and bearing gas. The experiment temperature was controlled at 25°C. The proton 90° pulse length was set to 4  $\mu\text{s}$ . The TMS was used as an external chemical shift reference. CP performance was optimized using 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt (DSS). Line broadening of 50 Hz was applied in all spectra.

## 3. Results and discussion

### 3.1. Thermogravimetric studies of the support silica

Thermogravimetric studies of the original silica were conducted to obtain information on the surface reactivity and thermal stability of the samples

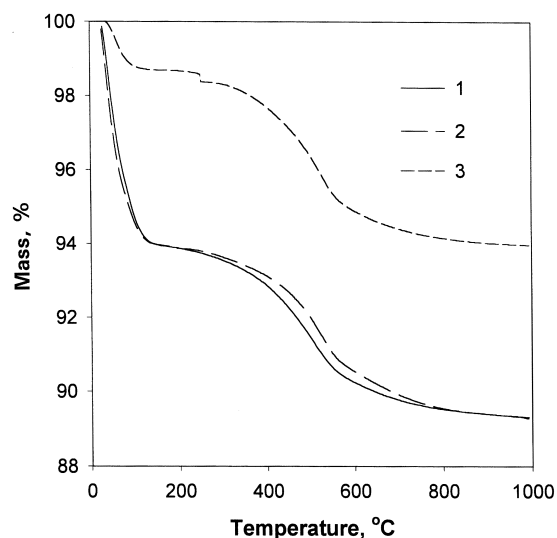


Fig. 1. Cumulative TGA curves for non-modified silica gel Luna: 1: regular TGA run, 2: isothermal equilibration at 180°C, 3: isothermal equilibration at 250°C. Note that the differences between TGA curves 1 and 3 in the temperature range between 25 and 200°C reflect different amounts of physically adsorbed water.

studied. The cumulative mass curves for non-modified Luna sample are shown in Fig. 1. The TGA curve 1 shows two distinct steps. The first step, starting at room temperature, corresponds to desorption of physically adsorbed water, while the second step, starting approximately at 250°C, reflects rather a complex process of decomposition of surface silanols accompanied by removal of structurally bonded water.

The sample mass at 250°C (i.e. without physically adsorbed water) was used as a reference to calculate the amount of water released in the second step of TGA. This amount calculated between 250 and 800°C was equal to 5.40  $\mu\text{mol}(\text{H}_2\text{O})/\text{m}^2$ , as determined from curve 1 (Fig. 1). An attempt to separate a contribution arising from structurally bonded water was undertaken in the next TGA run (curve 2), in which the sample was isothermally equilibrated at 180°C for 2 h. In another experiment (curve 3) the isothermal step was repeated at 250°C for 2 h. In this temperature range isothermal treatment should not affect the silanol coverage [4,14] and promote thermodesorption of structurally bonded water. However, in neither case the isothermal equilibration had a noticeable effect. On average Luna sample released  $5.40 \pm 0.03 \mu\text{mol}(\text{H}_2\text{O})/\text{m}^2$

between 250°C and 800°C as determined with respect to the sample weight at 250°C. Thermodesorption of  $5.40 \mu\text{mol}(\text{H}_2\text{O})/\text{m}^2$  corresponds to the surface silanol coverage of  $10.80 \mu\text{mol}(\text{OH})/\text{m}^2$ . Such high silanol coverage well exceeds an established theoretical limit of  $8 \mu\text{mol}(\text{OH})/\text{m}^2$  [13]. However, recently Chuang and Maciel proposed a new model of silica structure [15]. According to this model the silanol surface coverage may be as high as  $13 \mu\text{mol}(\text{OH})/\text{m}^2$ . Thus, in terms of this model  $10.80 \mu\text{mol}(\text{OH})/\text{m}^2$  may be an acceptable number.

### 3.2. Thermogravimetric studies of the modified silica gels

An important information on thermal stability of the derivatized silica samples can be obtained from their thermal analysis. A cumulative TGA curve of the freshly synthesized Luna-1.60 sample is shown in Fig. 2 (curve 1). A decrease in the sample weight from room temperature to approximately 200°C is related to thermodesorption of solvents from the silica surface. However, above 200°C the TGA curve of the sample exhibits sharp step indicating degradation of the sample. The corresponding DTG curve

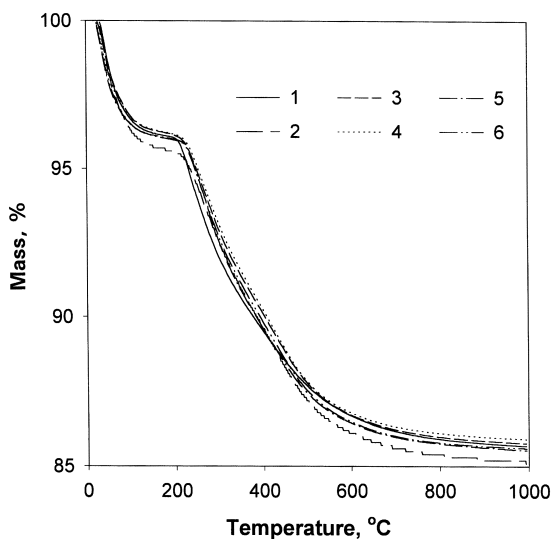


Fig. 2. Cumulative mass curves for modified silica gel Luna-1.60: 1: as synthesized washed with toluene, water, methanol, acetone, 2: washed with methanol, 3 and 4: washed with toluene, 5: washed with methanol, 6: washed with acetonitrile–water (50:50%, v/v) mixture.

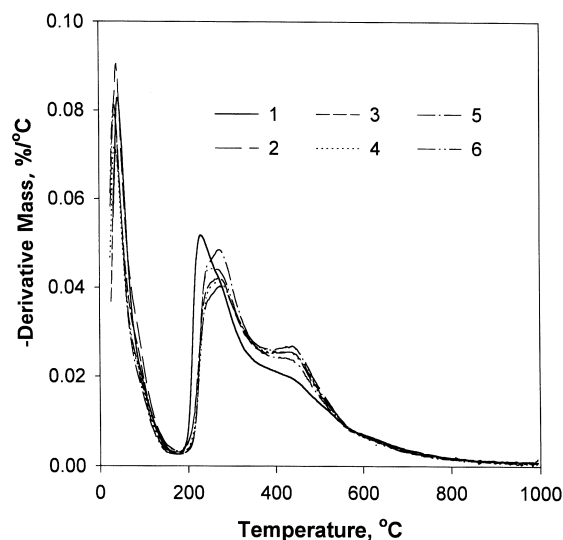


Fig. 3. Differential mass curves for modified silica gel Luna-1.60: 1: as synthesized washed with toluene, water, methanol, acetone, 2: washed with methanol, 3 and 4: washed with toluene, 5: washed with methanol, 6: washed with acetonitrile–water (50:50, v/v) mixture.

allows to distinguish two steps of the decomposition process (Fig. 3). The first step is approximately in the temperature range between 200 and 370°C, and the second step is in the range between 370 and 600°C. The onset of the first decomposition step starts at the temperature close to the boiling temperature of *n*-octyldimethylchlorosilane (222.5°C). Therefore, the appearance of the first decomposition peak was attributed to evaporation of the unbonded surface modifier, while the second decomposition step was clearly related to thermal decomposition of the chemically bonded octyl phase [16].

Accordingly, in order to remove the excess amount of unreacted silane the sample was washed with 250 ml of methanol and dried overnight in a vacuum oven at 110°C. The following day thermal analysis of the sample was performed. As can be seen from curve 2 shown in Figs. 2 and 3, further washing of the sample did not introduce significant changes in the character of the TGA and DTG curves. Consequently, washing of the sample followed by drying in the oven was repeated for Luna-1.60 with at least 300 ml portions of toluene, methanol and acetonitrile–water (50:50, v/v) mixture. However, such treatment of the sample had no

effect on its thermal stability as well as on the mass change between 200 and 600°C (see Fig. 2 and Fig. 3). This outcome suggested that modifier was strongly attached to silica, and at least two states of silane's attachment existed on the surface. In order to interpret this result it is necessary to consider a mechanism of reaction between chlorosilane and silica. A generalized mechanism of this reaction [5] consists of two steps. Initial step involves hydrolysis of chlorosilane by water molecules present on the surface of silica. In the following step the silanols formed in the hydrolysis step condense with surface hydroxyl groups producing strong Si–O–Si<sub>s</sub> bonds (s refers to support silica surface). Therefore, the low temperature DTG peak (200–370°C) could be related to the state of silane molecules, which did not completely react with surface silanols after the silane hydrolysis step. However, in order to obtain a suitable chromatographic packing it was necessary to achieve a uniform attachment of octyl ligands to the silica surface. According to literature reports on the silica modification with polyfunctional organosilane [5,6,11], a part of the hydrolyzed silane could remain physisorbed on the silica surface after modification. Therefore, a postreaction curing step may be required to facilitate condensation of silanols with surface hydroxyls. Thus, further studies of the derivatized samples were undertaken to investigate whether the postreaction curing step would enhance stability of the octyl phase.

The TGA analysis was modified with additional segment, which allowed for isothermal equilibration of the sample at 180°C for 2 h. The resulting cumulative and derivative mass curves for Luna-1.60 are shown in Figs. 4 and 5 (curve 7). The sample curing is reflected in the TG curve as a small step at 180°C, which accounts for ca. 0.5% of the total mass of the sample. As can be easily seen, the isothermal equilibration of the sample dramatically improved its stability. In contrast to the freshly synthesized sample (curve 1), the mass curve of the equilibrated sample does not inherit a sharp bent above 200°C. Accordingly, the corresponding DTG curve shows only one decomposition peak with a maximum at 480°C, which is related to thermal destruction of the chemically bonded phase. Notice that the overall weight loss in the temperature range from 180 to 600°C is essentially the same for as

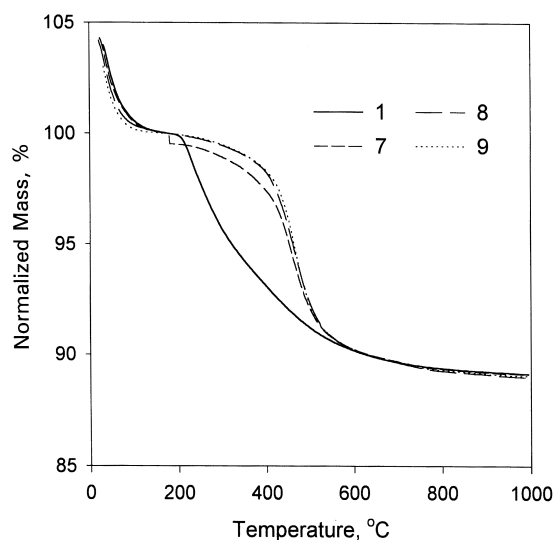


Fig. 4. Normalized cumulative mass curves for Luna-1.60 sample: 1: as synthesized, 7: equilibrated at 180°C, 8: sample left untouched for two weeks at ambient temperature, 9: sample after column packing. For better comparison cumulative mass curve of each sample was multiplied by the sample mass at room temperature and divided by the sample mass at 180°C.

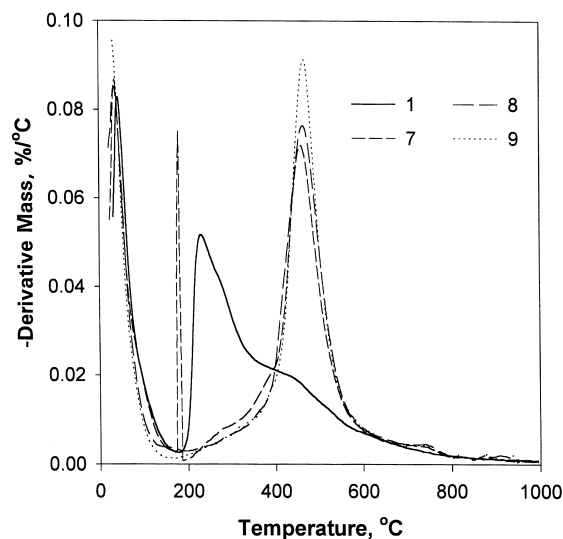


Fig. 5. Derivative mass curves for Luna-1.60 sample: 1: as synthesized, 7: equilibrated at 180°C, 8: sample left untouched for two weeks at ambient temperature, 9: sample after column packing.

synthesized and cured samples, except the weight loss of ca. 0.5% due to thermal equilibration of the sample. Thus, changes in the TGA spectra suggested that isothermal equilibration of the sample facilitated completion of the modification reaction. Similar trends were observed for the other samples, i.e. Luna-3.32 and Luna-1.20. It also was found that sample curing could be accomplished if equilibration step was performed at the temperature of 140°C for 2 h.

Additionally, in a parallel study, a part of the non-equilibrated Luna-1.60 sample was left in a vial at ambient temperature without any further treatment for a period of two weeks and after that time thermal analysis was repeated without equilibration step. Curve 8 in Figs. 4 and 5 demonstrates that modification can be completed even at a room temperature provided a sufficient reaction time is available.

More information on the physical state of octyl phase in a freshly synthesized sample was obtained from thermal analysis of Luna-1.20 sample. Contrary to the other samples, for freshly synthesized Luna-1.20, which had been washed with copious amount of protonic solvents (such as water, methanol), TGA analysis showed that the modifier could be removed. Thus, curve 1 in Fig. 6 corresponds to the unstable freshly synthesized sample. On the other hand, curve 2 corresponds to Luna-1.20 sample extensively washed with protonic solvents. Difference between curves 1 and 2 reflects the amount of hydrolyzed silane which was washed away from the silica surface. Thus, these experiments demonstrate the advantages of the curing process. Even though the surface species, which are present on the silica surface after the derivatization, can be removed after vigorous washing of the sample, this process is extremely difficult due to strong affinity of these species to the silica surface.

### 3.3. CP-MAS-NMR studies

Although it is accepted that a general mechanism of reaction between chlorosilane and surface hydroxyls consists of two stages (i.e. hydrolysis of chlorosilane followed by condensation of silanols with surface hydroxyls) [5], more detailed studies of the reaction mechanism often consider formation of

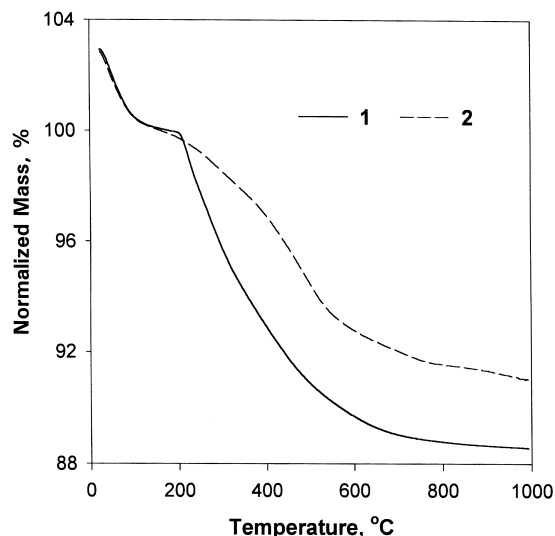


Fig. 6. Normalized cumulative mass curves for Luna-1.20 sample: 1: as synthesized, 2: sample after multiple washings (with toluene, water, methanol, acetone).

reaction intermediates which can either be physisorbed or chemically attached to the surface [17,18]. In order to differentiate between these two possibilities, the synthesis of the octyl phase was repeated. According to thermal analysis data, the freshly synthesized sample exhibited two DTG peaks between 200 and 600°C, and had a surface coverage comparable to Luna-1.60 sample. For this sample the  $^{29}\text{Si}$ -CP-MAS-NMR spectrum was recorded. As can be seen in Fig. 7, this spectrum is typical for monofunctionally derivatized silica gel [19]. The three peaks at  $-90$  ppm,  $-109$  ppm and  $-109$  ppm correspond to the signals of geminal silanol groups ( $Q_2$ ), isolated silanol groups ( $Q_3$ ) and siloxane groups ( $Q_4$ ), respectively. A single peak at 15 ppm corresponds to the signal of octyldimethylsilyl group (i.e. bonded phase). Other than that the spectrum of the freshly synthesized silica-based octyl phase contains no other peaks, which indicates that the appearance of the DTG peak between 200 and 370°C is related to species physically adsorbed on the silica surface. Therefore, it is logical to conclude that these species are the products of chlorosilane hydrolysis, which during the postreaction treatment condense with surface hydroxyls producing  $\text{Si-O-Si}_n$  bonds.

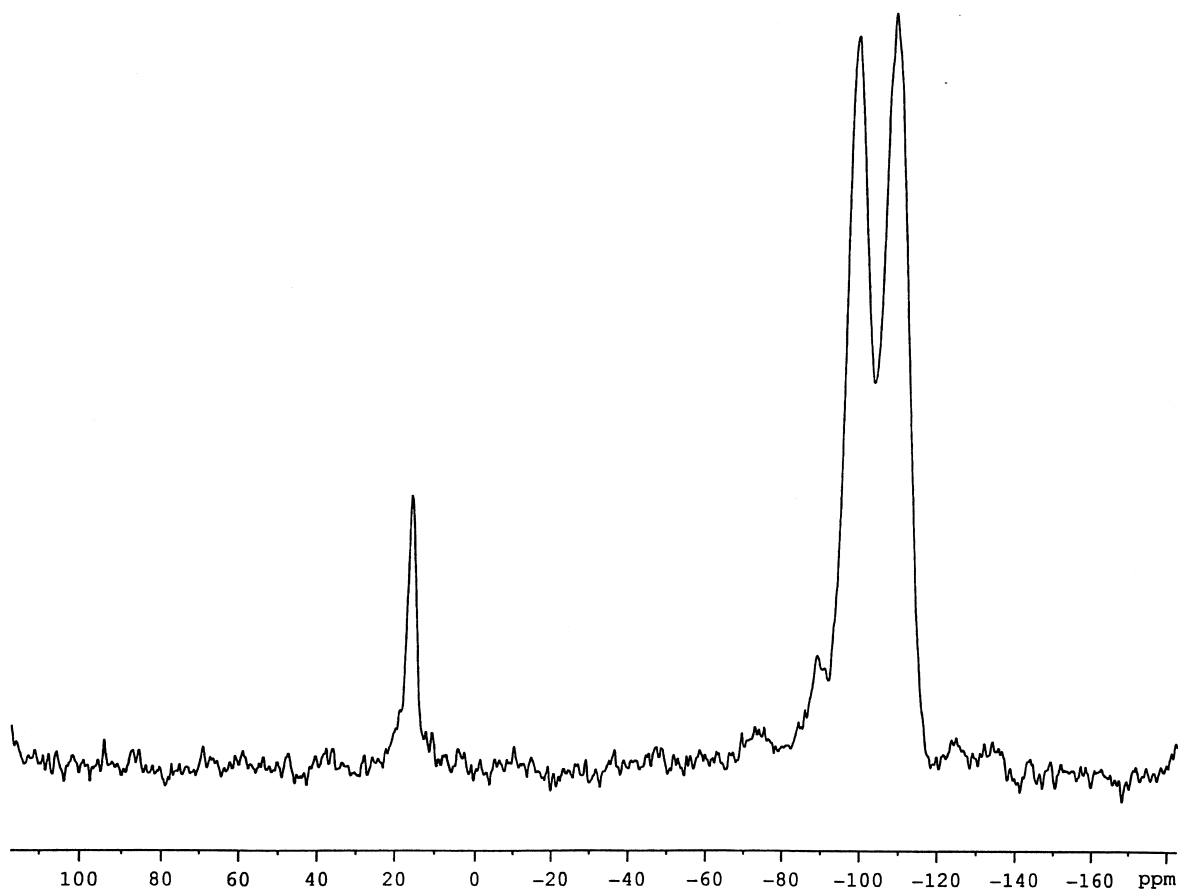


Fig. 7.  $^1\text{H}$ - $^{29}\text{Si}$ -CP-MAS-NMR spectrum of the freshly synthesized sample: 600 scans, contact time 12 ms.

#### 4. Conclusions

Chemically bonded phases of different surface coverages were synthesized using the same silica support. Their surface properties were characterized by means of thermogravimetry and solid-state NMR. Characterization of octyl phases by thermogravimetry revealed that at the end of modification procedure the silanizing agent was present on the surface in two states. In order to differentiate between these two states the  $^{29}\text{Si}$ -CP-MAS spectrum of the freshly synthesized octyl phase sample was recorded. The NMR studies of the freshly synthesized sample confirmed formation of the Si–O–Si<sub>s</sub> bonds between *n*-octyldimethylsilyl group and silica surface. However, these data did not provide evi-

dence for the presence of reaction intermediates chemically attached to the silica surface. Therefore, the appearance of the DTG peak between 200 and 370°C was attributed to thermodesorption of the hydrolyzed silane, which could be physically adsorbed on the silica surface via hydrogen bonding. As a result, additional post-reaction treatment was needed to complete the modification reaction in order to facilitate the condensation reaction between silanols and surface hydroxyl groups.

In addition, this work demonstrates an important distinction between modification of silica with long chain and short chain monochlorosilanes. As shown by Tripp and Hair [6], who studied modification of silica with trimethylchlorosilane, the postreaction curing essentially resulted in desorption of the

physically adsorbed trimethylsilanol species, which can be explained due to a relatively high vapor pressure of this moiety at the curing temperature (200°C). In the case of the silica derivatized with long alkyl chain organosilane, the vapor pressure of the corresponding silanol should be much lower compared to that of trimethylsilanol, subsequently, the curing process resulted in the improved thermal stability of the sample and greater amount of the octylsilyl species chemically attached to the surface. This result has important practical consequences since the curing process can be potentially useful to enhance the surface coverage of the synthesized chemically bonded phases.

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