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CHARACTERIZATION OF CHEMICALLY MODIFIED SILICA GELS BY ^{29}Si AND ^{13}C CROSS-POLARIZATION AND MAGIC ANGLE SPINNING NUCLEAR MAGNETIC RESONANCE

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SUMMARY

Chemically modified silica gels were prepared and examined by use of solid-state ^{13}C and ^{29}Si cross-polarization and magic angle spinning nuclear magnetic resonance spectroscopy. By this method, one can not only distinguish between various structural elements in the surface region, but also differentiate according to their mode of preparation. The results of the original manufacturing procedures for reversed-phase high-performance liquid chromatography materials and their subsequent treatment with trimethylsilylating reagents can be investigated. It is also possible to decide whether the solvents (*e.g.*, methanol) used in the preparation remain adsorbed at the surface or are completely removed by heat treatment. Further developments of this method of investigation may reveal the molecular mechanism of chromatographic separations.

INTRODUCTION

A wide variety of silica adsorbents with a narrow distribution of particle diameter, definite pore volume and reproducible specific surface area are commercially available. The applicability of such materials is strongly dependent on their surface properties. Chemical modification of the surface is usually achieved by bonding an appropriate organosilicon compound via the stable Si–O–Si–C moiety. These chemically bonded stationary phases have stimulated more recent development in the field of reversed-phase high-performance liquid chromatography (RP-HPLC). Especially organosilanes with terminal functional groups have been successfully used for chemical modifications.

A wide variety of specific functional groups can be introduced on to silica surfaces. The technique of surface modification developed for silica gels has also been applied to such different fields of chemistry as catalysis by supported metal complexes[1], photochemistry[2], electrochemistry[3] and triphase catalysis[4]. There is not yet a

method available that gives an exact and detailed picture of the chemical species formed on the surface. Therefore, reproducible batches of preparations of reversed-phase materials are difficult to obtain, and the observed variations of retention and selectivity during the use of reversed phases often cannot be explained.

Only limited information about the bonded species is available from the use of infrared (IR), far infrared (FIR) and difference techniques of IR spectroscopy[5-8]. Other methods used for the characterization of chemically modified silica gels are thermogravimetry, e.g., in combination with differential thermal analysis, and pyrolysis gas chromatography–mass spectrometry. Another possibility is the hydrolytic cleavage of the Si–C bonds. These methods have the disadvantage that they are accompanied by the destruction of the chemically bonded material.

More powerful methods for the characterization of chemisorbed compounds are those in the field of solid-state nuclear magnetic resonance (NMR) spectroscopy. In the solid state, the line width is increased owing to dipole–dipole interactions and the anisotropy of the chemical shift tensor. Dipolar decoupling[9] in combination with magic angle spinning (MAS)[10], however, results in spectra that show resolutions comparable to those of high-resolution spectra. The long relaxation time of ^{13}C and ^{29}Si nuclei in the solid state is reduced by the recently introduced cross polarization (CP)[11,12]. Because CP efficiency is dependent on the Si–H distance, internal Si atoms do not contribute to the CP–MAS spectrum.

Up to the present, ^{13}C NMR spectroscopy with cross-polarization and magic angle spinning (^{13}C CP–MAS NMR) has been mainly used for the investigation of fossil fuels[13] and polymers[14]. Only a few data have been reported for ^{13}C NMR[15-17] and ^{29}Si NMR measurements[18-20] on silica gels modified with organosilanes. For further improvement of our recent investigation of on-line coupling of HPLC and NMR[21], we have prepared silica samples modified with a variety of organofunctional silanes and studied these phases by means of NMR spectroscopy. Both ^{13}C and ^{29}Si NMR spectroscopy[22] seemed very promising for obtaining information on different structural elements of the surface. The results obtained from measurements of modified silica gels prepared in our laboratory[23,24] were also used to characterize a number of commercial reversed-phase HPLC materials.

EXPERIMENTAL

The ^{29}Si and ^{13}C NMR spectra were obtained on a Bruker CXP-300 Fourier transform NMR spectrometer. Samples of 100–200 mg were measured in 6.3 mm I.D. rotors made of boron nitride (for ^{13}C spectra) or of Delrin (for ^{29}Si spectra). CP–MAS was used with alternative inversion of the 90° pulse phase. The proton 90° pulse length was 4.5 μsec. In the case of ^{29}Si contact times of 5 msec and repetition times of 4–6 sec were used. For ^{13}C, the contact times were 3 msec and repetition times 4–6 sec. The spinning speed was between 3.5 and 5 kHz; hence side bands do not appear for those compounds with a rather low anisotropic chemical shift tensor.

The variation of the magic angle was checked with glycine between the experiments; the line width of the carbonyl signal never exceeded 30 Hz. For ^{13}C experiments the chemical shifts were referenced to tetramethylsilane by using the carbonyl signal of glycine as a secondary standard (170.09 ppm). For ^{29}Si data, the referencing of Engelhardt et al.[18] was adopted. No magic angle check for ^{29}Si was

necessary, as the broad-band probe tuned between deuterium and ^{13}C without modification.

The inherent stability of cryomagnets allows measurements without lock or internal reference standard.

Materials

The silica gels used for surface modifications are commercially available. LiChroprep Si60 (BET surface area, S_{BET} = 500 m^2/g; particle diameter, d_p = 15–25 μm) and Si 60 H (S_{BET} = 500 m^2/g, d_p = 15 μm) were purchased from Merck (Darmstadt, G.F.R.). Polygosil 60 (S_{BET} = 500 m^2/g, d_p = 5–20 μm) was obtained from Macherey, Nagel & Co. (Düren, G.F.R.).

The sources of other reagents were as follows: butyllithium (as a 15% solution in n-hexane), Metallgesellschaft (Frankfurt, G.F.R.); trichlorosilane, Fluka (Buchs, Switzerland); dimethylchlorosilane and 3-aminopropyltriethoxysilane, EGA (Steinheim/Albuch, G.F.R.); and dimethyldichlorosilane, trimethylchlorosilane and hexamethyldisilazane, Merck. 10-Undecenyl-1-dimethylchlorosilane was prepared from 11-chloroundecene-1 and dichlorodimethylsilane by Grignard cross-coupling; n-butyl-1-dimethylchlorosilane was prepared by reaction of n-butyllithium with dichlorodimethylsilane. The silanes bearing an ester group as precursor for a hydroxyl group were obtained by homogeneously catalysed hydrosilylation (H$_2$PtCl$_6$–2-propanol) of the corresponding olefins with trichlorosilane or chlorodimethylsilane.

The following commercial reversed-phase materials were investigated: RP-18, 10 μm (Merck); Nucleosil 5 C$_{18}$ and 5 C$_8$ (Macherey, Nagel & Co.); ODS-Hypersil (Shandon, Runcorn, Great Britain); and Spherisorb ODS 2 (Phase Separations, Queensferry, Great Britain).

The silica samples were dried before the modification in high vacuum at 170°C for 48 h. After this pre-treatment the adsorbents were stored under an argon atmosphere in Schlenk tubes. If not otherwise noted, all subsequent operations were carried out under argon using the Schlenk technique to avoid any contact with impurities and moisture from the air. The solvents were purified according to known procedures and distilled in an inert gas atmosphere.

Procedures

n-Butyl-1-dimethylsilylsilica (1), 10-undecenyl-1-dimethylsilylsilica (2), 11-acetoxyundecyl-1-dimethylsilylsilica (3), 10-carbomethoxydecyl-1-dimethylsilylsilica (4) and 11-acetoxyundecyl-1-silylsilica (8) were prepared according to the following general procedure. A 10-g sample of silica gel Si 60 H was suspended in 150 ml of toluene and 30 mmol of the corresponding halogenosilane was slowly added to the suspension. The mixture was stirred at 80°C for 24 h while a slight stream of nitrogen was passed through. The silica derivative was filtered off and the excess of silane was extracted with toluene. Residual silanol groups were capped with an excess of TMCS–HMDS (molar ratio 1:2) according to known procedures[25].

The derivatives 1, 2, 3 and 8 and the trimethylsilylated compounds 3-TMS, 4-TMS and 8-TMS were additionally washed with methanol, whereas sample 4 was extracted only with toluene.

The silica derivatives were heated under high vacuum at the temperatures given in the table of elemental analyses (Table I).

TABLE I

PROPERTIES OF SAMPLES 1–4 AND 8

Sample No.	Carbon content (% C)	Surface coverage (mmol/g)	Drying temperature (°C)
1	3.04	0.42	120
2	7.26	0.47	20
3	10.52	0.58	120
3-TMS	12.56		120
4	11.61	0.64	120
4-TMS	13.31		120
8	9.91	0.55	120
8-TMS	11.45		20

A: PREPARATION OF REVERSED-PHASE SILICA GELS

Fig. 1.

B: END-CAPPING

X = OH,-O-Alkyl, -O-Si-O-

X = CH₃ (silane remains unchanged)

R = functional alkyl chain
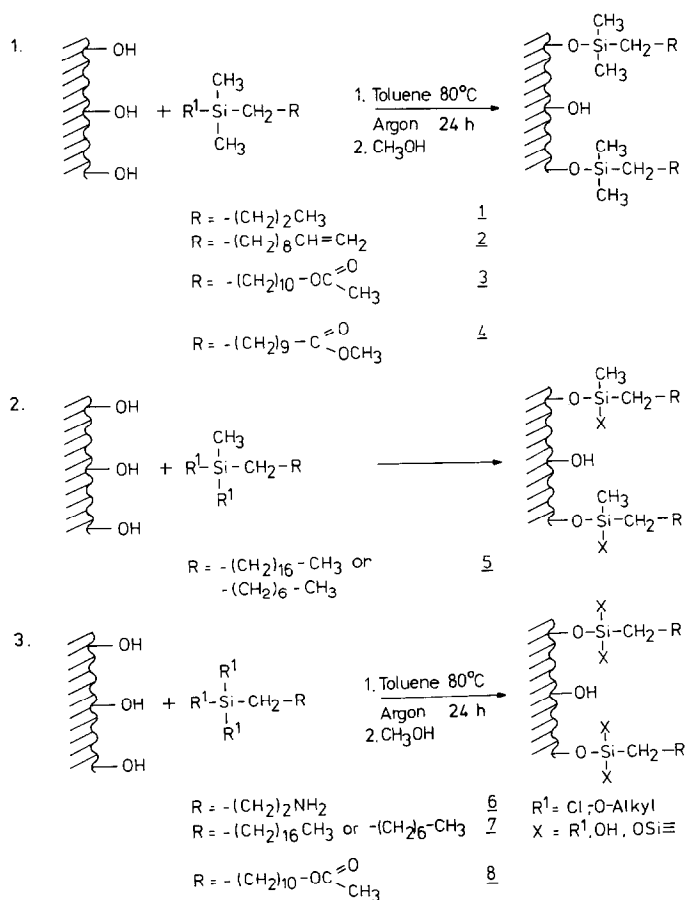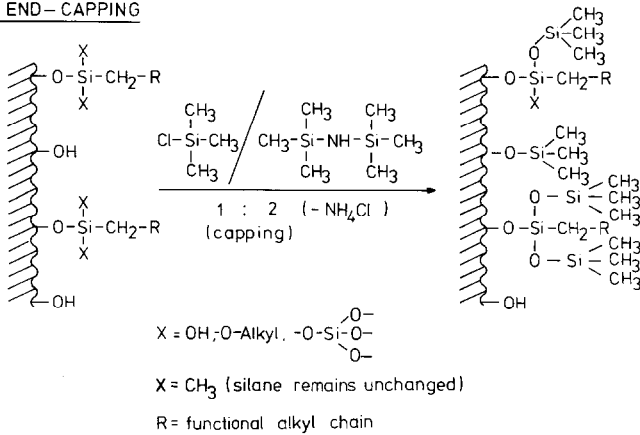
C: DERIVATIZATION OF CHEMICALLY BONDED PHASES

1.

2.
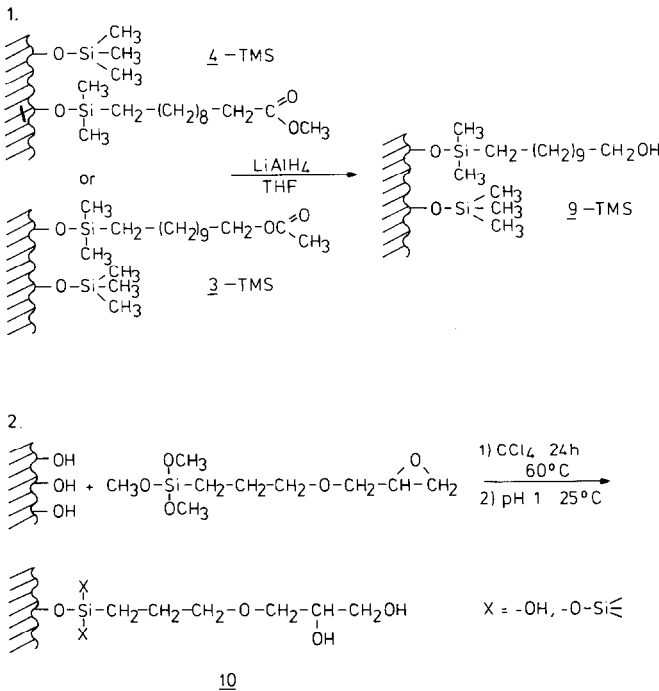
Fig. 1. Reaction scheme for the preparation of chemically modified silica gels.

11-Hydroxyundecyl-1-dimethylsilylsilica (9) (capped 9-TMS) was prepared as follows. A 300-mg amount of lithium tetrahydridoaluminate were suspended in 30 ml of tetrahydrofuran (THF). The filtrate of this suspension was added dropwise at 10°C to 7 g of 3-TMS or 4-TMS suspended in 75 ml of THF. After complete addition the mixture was stirred for 1 h at 20°C. The silica was separated from excess of reducing reagent and washed with THF. After decomposition of the aluminium alco-
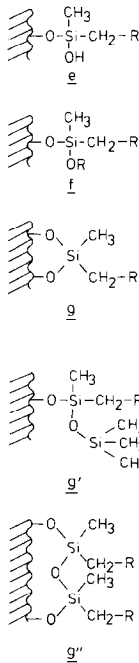
E. BAYER *et al*

A: PURE SILICA GEL

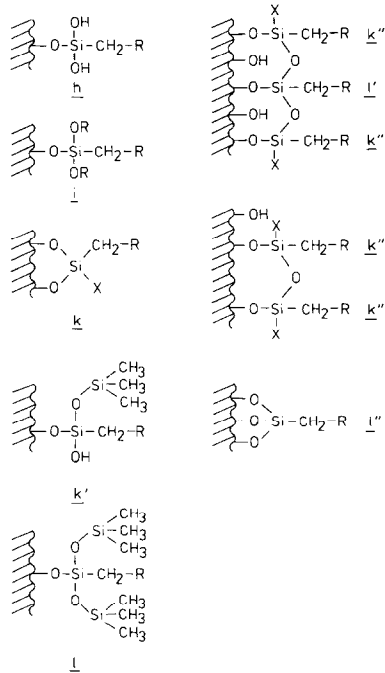a   b
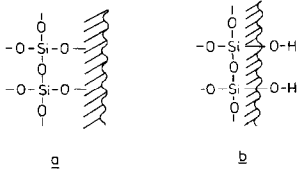
B: SURFACE OF SILICA GEL AFTER TREATMENT WITH
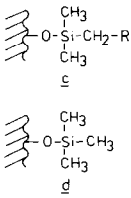
MONOFUNCTIONAL SILANE   DIFUNCTIONAL SILANE   TRIFUNCTIONAL SILANE

c   e   h   k″   l′   k″

d   f   i   k″

g   k   k″   k″

g′   k′   l″

g″   l

C: CHEMICALLY BONDED ALKYLCHAIN

A   A′   A″

A‴

1   2   3   4 – 15   16   17   18

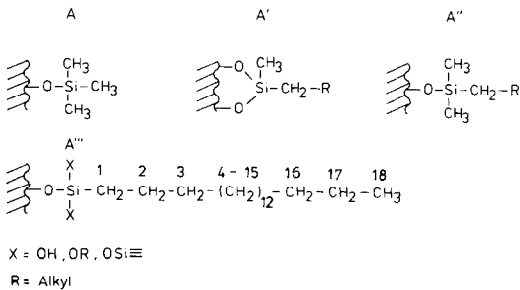$X = OH, OR, OSi\equiv$

R = Alkyl

Fig. 2. Structural elements at the surface of bonded stationary phases.

holate in THF by careful addition of 10^{-2} N hydrochloric acid, the silica sample was washed repeatedly with water (until the filtrate was free from chloride) and finally with methanol. The reduced silica gel was treated at 150°C under high vacuum for 20 h. The IR spectrum showed no absorption in the C=O region.

The elemental analysis was as follows: 11.78% C (reduction of 3-TMS) and 10.70% C (reduction of 4-TMS).

3-Aminopropyl-1-silylsilica   (6)   and   1,2-dihydroxypropoxy-3-propyl-1-silylsilica (10) were prepared according to known procedures[26]. Their elemental analyses were as follows: (6) 2.5% C, 0.7% N, specific coverage 0.69 mmol/g; (10) 6.4% C, specific coverage 0.89 mmol/g.

RESULTS AND DISCUSSION

The different types of surface modifications described are shown in Fig. 1. The corresponding structural elements that are possible at the surface of silica gel after silanization are depicted in Fig. 2.

In the ^{29}Si CP–MAS NMR spectrum of pure silica gel Si 60 (Merck) we observed two resonances, at -100 and -110 ppm, which correspond to tetraoxo-coordinated framework silicon (structure a) and surface silanol groups (structure b)[27] as shown in Fig. 2. Sindorf and Maciel[20] interpreted the shoulder at -90 ppm in terms of geminal silanol groups. However, we are not able to confirm their result. A peak due to these geminal silanol groups, if at all present and then in only very low concentration, was not detectable in our measurements.
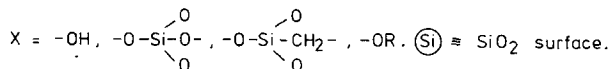
The data obtained for samples prepared by ourselves are summarized in Tables II and III. First we consider the reaction of monofunctional silanes with silica gel (reaction 1 in Fig. 1). The ^{29}Si CP–MAS NMR spectrum of n-butyldimethylsilylsilica (1) is shown in Fig. 3. Compared with pure silica gel, a new resonance of the silicon atom attached to the surface appears at $+12.3$ ppm. This indicates the existence of structural element c (Fig. 2). The structure of the alkyl chain is obtained from the ^{13}C CP–MAS NMR spectrum shown in Fig. 4.

The assignment for the solid-state spectrum of this silica derivative is based on the proton-coupled ^{13}C NMR spectrum of the silane recorded in solution at 100.62 MHz. Carbons 2 and 3 are distinguishable by their different coupling patterns: C-2 exhibits a triplet of triplets ($^{1}J = 125.4$ Hz; $^{2}J = 3.6$ Hz) whereas C-3 shows a triplet of quartets ($^{1}J = 126.4$ Hz; $^{2}J = 5.4$ Hz). Comparing the ^{13}C chemical shifts of compound 1 in the solid state and that of the silane we have to consider the chemical environment of the silicon atom due to the attachment of silicon to one chlorine atom in ClSi$(CH_3)_2(CH_2)_3CH_3$ (Table II) and to a surface silicon group. The difference of carbon 1 (Si–CH$_2$) chemical shifts is about 3 ppm. The chemical shifts of carbons 2 and 3 are not severely affected. However, the methyl resonance (C-4) is shifted to higher field by about 3 ppm.

The assignments of the ^{13}C CP–MAS NMR spectra of the other silica gels modified with monofunctional long-chain alkylsilanes are based on the considerations mentioned above. For instance, the Si–CH$_2$ carbon absorbs between 17 and 18.5 ppm (in the corresponding halogenosilane this carbon atom appears at 19–22 ppm). The other carbon atoms of the alkyl chain are only slightly affected by variation of the environment at the silicon atom [this is demonstrated in the spectrum of trimethylsilylated 11-hydroxyundecyl-1-dimethylsilylsilica (9-TMS) in Fig. 5].

TABLE II

CP–MAS NMR DATA FOR SILICA GEL PHASES

A = Structural elements shown in Fig. 2.

$$X = -OH, \quad -O-\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}-O-, \quad -O-\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}-CH_2-, \quad -OR. \quad \textcircled{Si} \equiv SiO_2 \text{ surface.}$$

Compound	^{13}C CP–MAS NMR data (ppm)
1	$A''\diagup CH_3$ 1 2 3 4 $\textcircled{Si}-O-\underset{\diagdown CH_3}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-CH_3$ (−OCH₃) −3.4 16.0 25.4 24.1 10.6 44.0/50.0
2	$A''\diagup CH_3$ 1 2 3 4−8 9 10 11 $\textcircled{Si}-O-\underset{\diagdown CH_3}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-(CH_2)_5-CH_2-CH=CH_2$ (−OCH₃) −1.5 18.1 23.0 33.1 30.0 33.1 137.1 114.4 44.3/50.1
9-TMS	$A+A''\diagup CH_3$ 1 2 3 4−8 9 10 11 $\textcircled{Si}-O-\underset{\diagdown CH_3}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-(CH_2)_5-CH_2-CH_2-CH_2-OH$ * −0.5 17.9 23.1 32.9 28.9 25.6 32.9 62.3
	$A''\diagup CH_3$ 1 2 3 4−8 9 10 11 O $\textcircled{Si}-O-\underset{\diagdown CH_3}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-(CH_2)_5-CH_2-CH_2-CH_2-O-\overset{\parallel}{C}-CH_3$ −0.5 17.0 22.6 33.0 28.7 25.7 30.0 65.1 20.3
8-TMS	$A+A''\diagup X$ 1 2 3 4−8 9 10 11 O $\textcircled{Si}-O-\underset{\diagdown X}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-(CH_2)_5-CH_2-CH_2-CH_2-O-\overset{\parallel}{C}-CH_3$ * (−OCH₃) −1.0 13.4 22.6 33.0 28.9 25.4 31.7 63.6 19.4 44.5/50.2
4	$A''\diagup CH_3$ 1 2 3 4−8 9 10 O $\textcircled{Si}-O-\underset{\diagdown CH_3}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-(CH_2)_5-CH_2-CH_2-\overset{\parallel}{C}-O-CH_3$ −1.7 16.6 22.3 32.6 28.3 23.5 32.6 50.7
10	$A'''\diagup X$ 1 2 3 4 5 6 $\textcircled{Si}-O-\underset{\diagdown X}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-O-CH_2-\underset{\underset{OH}{\mid}}{CH}-CH_2-OH$ 9.6 22.3 71.2 71.2 71.2 63.1
6	$A'''\diagup X$ 1 2 3 $\textcircled{Si}-O-\underset{\diagdown X}{\overset{\diagup}{Si}}-CH_2-CH_2-CH_2-NH_2$ 10.0 26.9 43.9

^{29}Si CP–MAS NMR data (ppm)

Samples 1 and 3	Sample 6	Sample 10
+13.2 d	−56.6 k + k''	−48.0 h
−100.8 b	−100.2 b	−53.2 k + k''
−100.5 a	−109.9 a	−66.2 l'
		−100.2 b
		−108.9 a

* Samples containing trimethylsilyl groups attached to the surface.

TABLE III

^{13}C CHEMICAL SHIFTS (ppm) OF ORGANOFUNCTIONAL SILANES, WHICH WERE USED IN THE SURFACE MODIFICATION (FIG. 1)

The assignments are based on proton coupled spectra.

```
      CH3    1      2      3      4      5      6      7
Cl - Si  - CH2 -CH2 - CH2 - CH2 - CH2 - CH2 - CH3
      CH3
      1,7    19.0   23.0   33.0   28.9   31.8   22.7   14.0


      CH3    1      2      3      4 - 8          9      10     11
Cl - Si  - CH2 - CH2 - CH2 - (CH2)5  -  CH2 - CH = CH2
      CH3
      1,6    19.2   23.4   34.2   29.9/29.3/29.6  33.3   139.1  114.5


      CH3    1      2      3      4 - 8        9      10     11     12 O 13
Cl - Si  - CH2 -CH2 -CH2 -(CH2)5  -  CH2 -CH2 -CH2 -O - C -CH3
      CH3
      1,5    18.8   22.9   32.8   29.4/29.1/28.5  25.8   29.1   64.4   170.8  20.8


      Cl     1      2      3      4 - 8        9      10     11     12 O 13
Cl - Si  - CH2 - CH2 - CH2 - (CH2)5  -  CH2 -CH2 -CH2 - O - C -CH3
      Cl
             22.1   24.2   31.6   29.2/28.8/28.5  25.8   29.2   64.4   170.8  20.8


      CH3    1      2      3      4 - 7        8      9      O 10   11
Cl - Si  - CH2 -CH2 -CH2 -(CH2)4  -  CH2 - CH2 - C - O -CH3
      CH3
      1,5    18.8   22.8   32.7   29.3/29.0      24.8   33.9   174.0  51.1


      CH3    1      2      3      4
Cl - Si  - CH2 -CH2 - CH2 - CH3
      CH3
      1,6    18.9   26.3   25.5   13.8


      CH3    1      2      3      4 - 15       16     17     18
Cl - Si  - CH2 - CH2 - CH2 - (CH2)12  -  CH2 - CH2 - CH3
      CH3
      1,7    19.3   23.5   33.5   29.8/30.2/30.9/31.5  32.5   23.2   14.4


                     1      2      3
(C2H5O)3-Si  -  CH2 - CH2 - CH2 - NH2      ( -OCH2 -      -CH3 )
                     7.0    26.6   44.5                   57.7      17.6


                     1      2      3      4      5  O  6
(CH3O)3-Si  -  CH2 - CH2 - CH2 - O - CH2 - CH2 -CH2      ( -OCH3 )
                     4.7    22.3   72.8          70.9   50.1   43.4      49.3
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Further, the resonance of a terminal methyl group is shifted to higher fields by reducing the chain length from 17 to 3 methylene units. Thus the chemical shift of the methyl group in octadecylsilica gels is 12.5 ± 0.4 ppm, in octylsilica gels it appears at 11.9 ppm and in butylsilica gel at 10.6 ppm. This additional shielding may be due to an increased steric interaction between the methyl group and the silica surface with decreasing chain length.
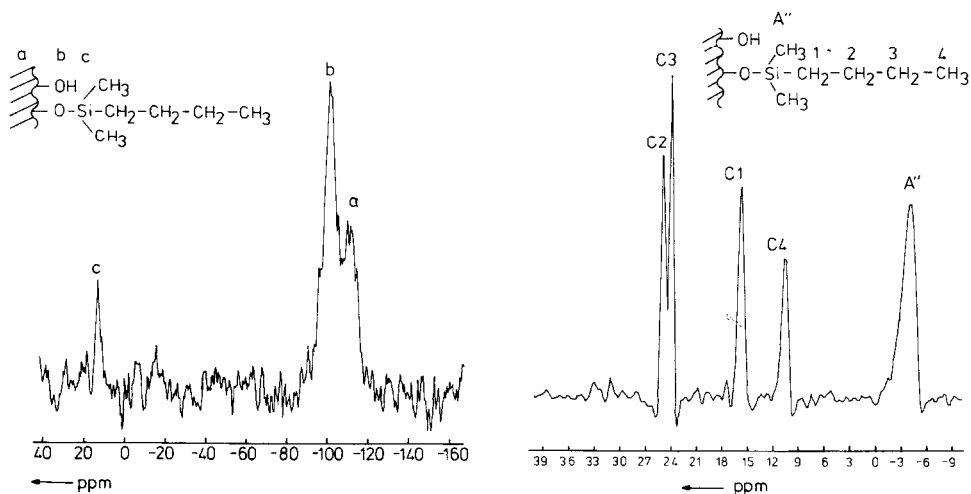
Fig. 3. 59.61 MHz ^{29}Si CP–MAS NMR spectrum of the reaction product of n-butyldimethylchlorosilane with silica gel (1).

Fig. 4. 75.46 MHz ^{13}C CP–MAS NMR spectrum of the reaction product of n-butyldimethylchlorosilane with silica gel (1).

In general, monofunctional silanes are easily identified by the absorption of the Si–CH$_3$ group between – 3.4 and 0.5 ppm which is absent in samples modified with trifunctional silanes. It should be noted that the ^{13}C CP–MAS NMR absorptions due to trimethylsilyl and alkyldimethylsilyl groups cannot be resolved. This difficulty also exists in ^{29}Si CP–MAS NMR spectroscopy. The presence of trimethylsilyl groups after end-capping is recognized qualitatively from the difference between the intensities of the ^{13}C signal of about 0 ppm of capped and uncapped material. The ^{13}C resonance of the Si–CH$_3$ group in a bonded monofunctional silane is found at 2 ppm higher field than for the corresponding halogenosilane in the liquid state.

By use of ^{13}C NMR spectroscopy it is possible to distinguish between the different types of surface bonding, which are dependent on the functionality of the silane used in the modification. For example, the ^{13}C CP–MAS NMR spectrum of end-capped 11-acetoxyundecyl-1-silylsilica (8-TMS) [this sample is readily obtained from reaction of silica gel with Cl$_3$Si(CH$_2$)$_{11}$OCOCH$_3$ and subsequent treatment with TMCS–HMDS (for details see experimental)] is depicted in Fig. 6. The carbon atom directly attached to the silicon atom gives rise to an absorption at 13.4 ppm (22.1 ppm in the trichlorosilane). The chemical shift of carbon 1 is found at 4 ppm lower field in a bonded monofunctional than in a trifunctional silane. A much better distinction of the various binding sites is possible by use of ^{29}Si NMR spectroscopy.

In the ^{29}Si CP–MAS NMR spectra of compounds 6 and 10 additional resonances compared with pure silica gel are observed at − 56.6 and − 53.2 ppm. This corresponds to the new silicon atom, introduced to the surface by reaction of silica gel with the trialkoxysilane. According to the literature[18,27], the chemical shift values found in the solid state are in good agreement with those measured in solution. Therefore, the position of the new resonance is indicative of a predominant coupling of the silane as a bidentate ligand. We conclude that the structural elements i, k and l′
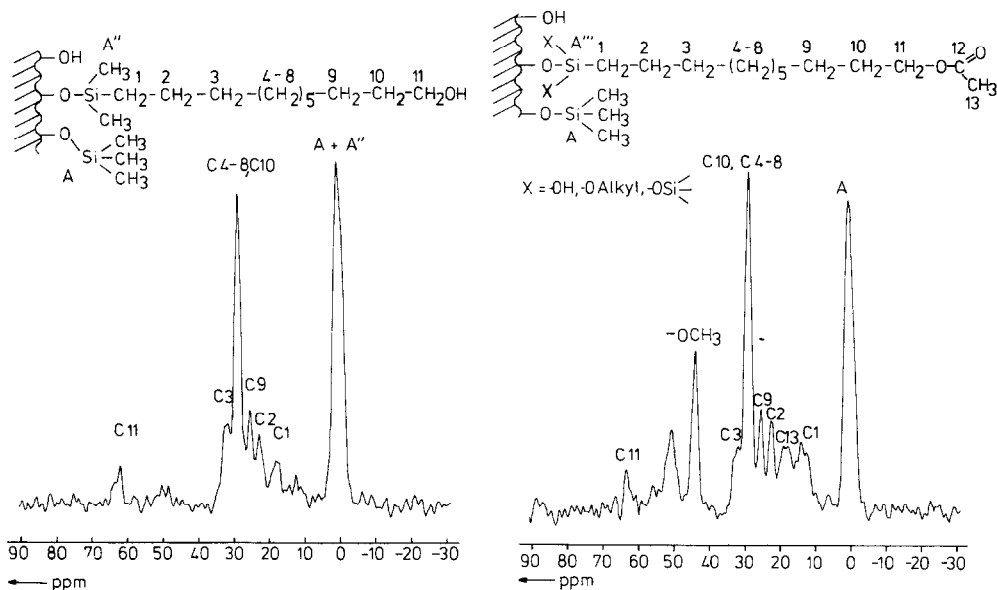
Fig. 5. 75.46 MHz ^{13}C CP–MAS NMR spectrum of the reaction product of 11-acetoxyundecyl-1-dimethylchlorosilane with silica gel, after end-capping and reduction with lithium tetrahydridoaluminate (9-TMS).

Fig. 6. 75.46 MHz ^{13}C CP–MAS NMR spectrum of the reaction product of 11-acetoxyundecyl-1-trichlorosilane with silica gel, after end-capping (8-TMS).

(Fig. 2) are present at the surface. The main peak at -53.2 ppm is assigned to element k. This is consistent with the reaction of *two* Si–OR groups with the surface. The weaker peak at -46 ppm is due to reaction of *one* Si–OR group and the peak at -66 ppm is consistent with poly- or oligolayer formation. Also the coupling of adjacent modifier units by Si–O–Si linkages cannot be excluded. This interpretation was also proposed by Sindorf and Maciel[20], who studied the reaction of Cl_3SiCH_3 with silica gel and followed the hydrolysis of unreacted Cl–Si groups by use of ^{29}Si NMR spectroscopy.

Further information about the structure of the alkyl chain after coupling at the surface is obtained from the ^{13}C CP–MAS NMR spectrum of 10 (Fig. 7). Owing to the absence of an absorption at 50 ppm we conclude that the silica derivative does not contain a methoxy group.

The data for 6 indicate that no alkoxy groups remain after the reaction of silica gel with 3-aminopropyltriethoxysilane. It can be seen from Fig. 7 that the oxirane ring of the glycidylsilica is completely hydrolysed (see Table III). The resonance of C-1 in silica samples 6 and 10 prepared by use of trifunctional short-chain silanes appears at about 10 ppm. These results demonstrate that the resonances of C-1 and of the silicon atom of the chemically bonded silane are sensitive indicators for the type of the structural elements present in the surface region. If, in addition, the other resonances of the organic residue are measured, the structure of bonded phases is easily elucidated.

In the same way, we have used the combination of ^{29}Si and ^{13}C NMR spectros-copy to obtain insight into structural details of commercial reversed-phase materials. The RP-8 and RP-18 materials can be distinguished by means of ^{13}C NMR spectros-copy. The functionality of the silane is obtained from the ^{29}Si NMR shift values. The structural elements which can be built up during the chemical modification are shown in Fig. 2. The ^{29}Si and ^{13}C NMR spectra of some commercial reversed phases are presented in Figs. 8–10. The chemical shift values are given in Tables IV and V.

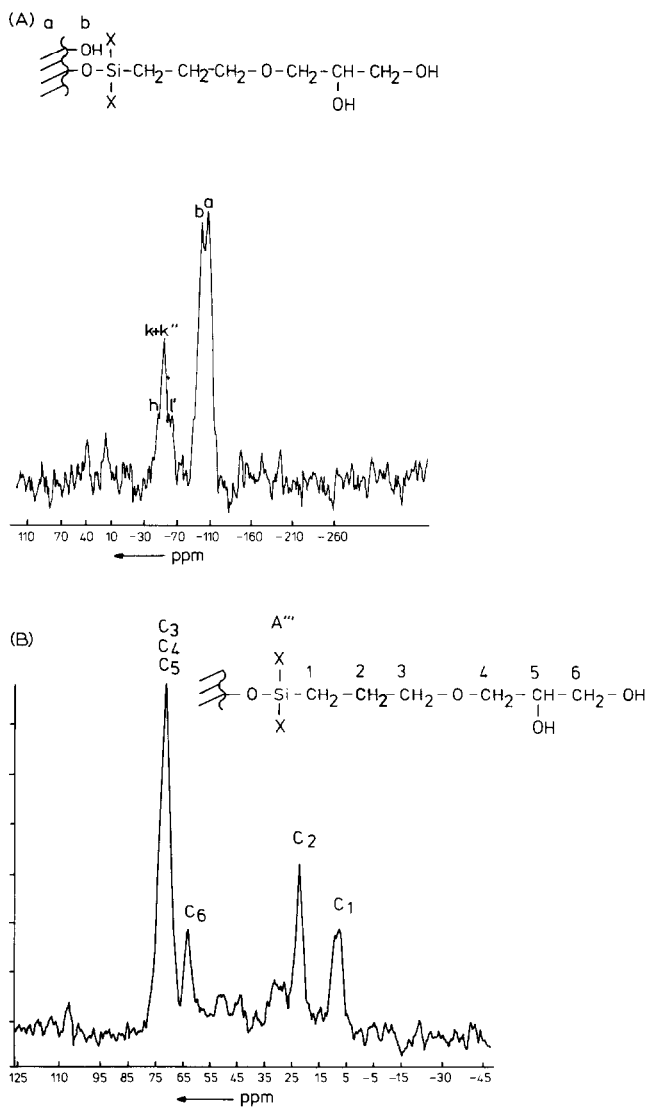From the data obtained we have drawn the following conclusions. Most of the

Fig. 7. (A) 59.61 MHz ^{29}Si CP–MAS NMR spectrum of the reaction product of 1,2-epoxy-3-propoxypropyltrimethoxysilane with silica gel (10). (B) 75.46 MHz ^{13}C CP–MAS NMR spectrum of the reaction product of 1,2-epoxy-3-propoxypropyltrimethoxysilane with silica gel (10).
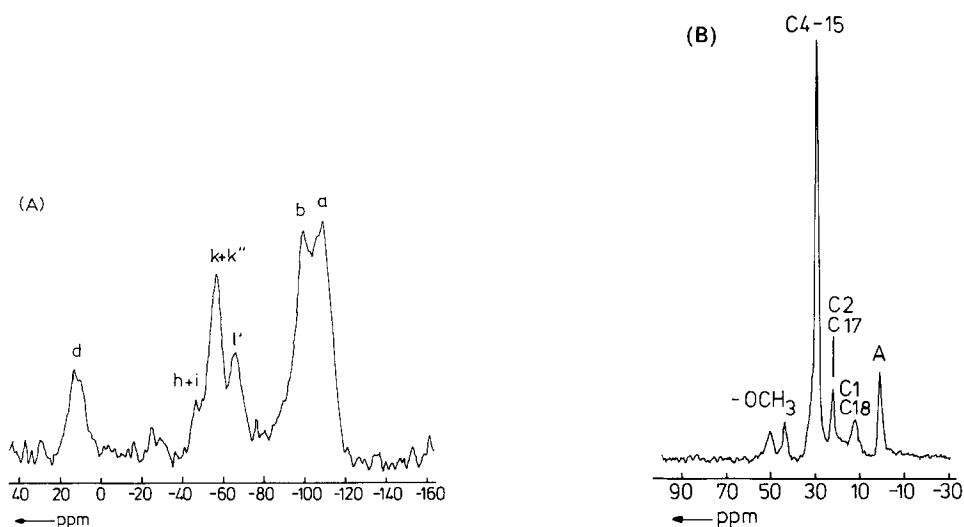
Fig. 8. (A) 59.61 MHz ^{29}Si CP–MAS NMR spectrum of Spherisorb ODS 2 (Phase Separations). (B) 75.46 MHz ^{13}C CP–MAS NMR spectrum of Spherisorb ODS 2 (Phase Separations).

materials investigated in this work were prepared by reaction of silica gel with trial-koxyalkylsilanes. The use of trichloroalkylsilanes would have the disadvantage of decreasing,the specific surface area. This effect is attributed to the cleavage of siloxane linkages by hydrogen chloride which is evolved during the modification. In general, the following structural elements (Fig. 2) are detectable in reversed phases derived from trifunctional alkylsilanes: i (-48 ppm), k and k'/k'' (-57 ppm) and l' (-66 ppm).
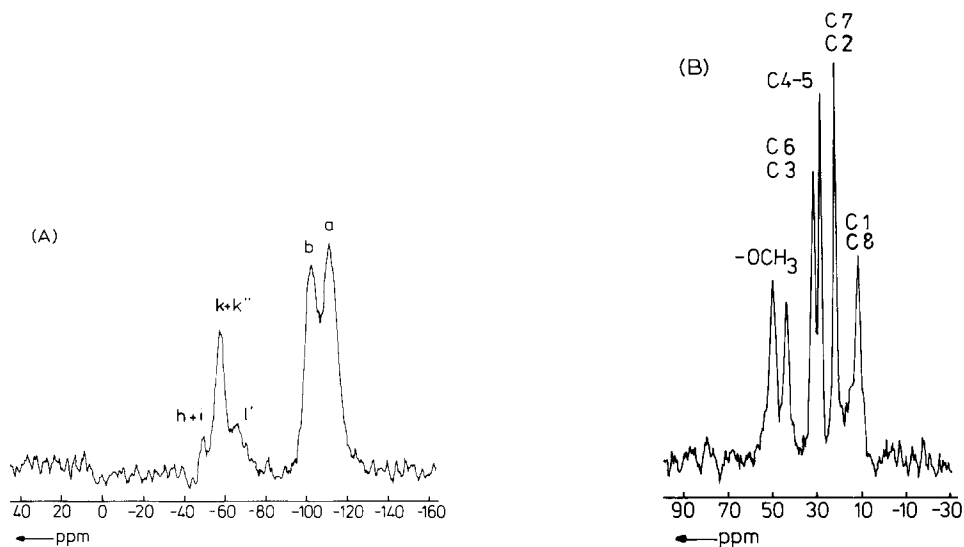

Fig. 9. (A) 59.61 MHz ^{29}Si CP–MAS NMR spectrum of Nucleosil 5 C$_8$ (Macherey, Nagel & Co.). (B) 75.46 MHz ^{13}C CP–MAS NMR spectrum of Nucleosil 5 C$_8$ (Macherey, Nagel & Co.).
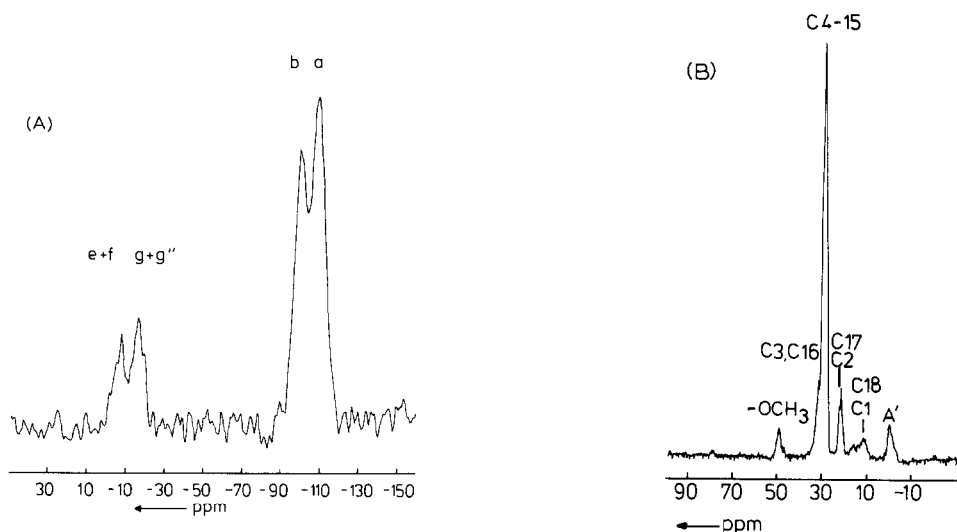
Fig. 10. (A) 59.61 MHz ^{29}Si CP–MAS NMR spectrum of RP-18, 10 μm (Merck). (B) 75.46 MHz ^{13}C CP–MAS NMR spectrum of RP-18, 10 μm (Merck).
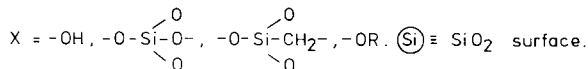
Elements designated by the same letter are not resolved in the spectra. Thus we are not able to distinguish between dimers at the surface and an oligolayer. However, we can clearly separate monolayers from condensed silane units. A subsequent treatment with trimethylsilylating reagents is indicated by an additional ^{29}Si resonance at + 12.0–13.0 ppm. Thus we find that the RP-18 materials obtained from Phase Separations (Spherisorb ODS 2), Shandon (ODS-Hypersil) and Macherey, Nagel & Co. (Nucleosil C_{18}) are subjected to end-capping. The Macherey, Nagel & Co. phase Nucleosil C_8, however, was not trimethylsilylated. In contrast to these phases, Merck uses difunctional silanes, e.g., dimethoxy- or diethoxymethyloctadecylsilane, for the manufacture of reversed phases (reaction 2, Fig. 1). The structural elements expected for this type of silane are e, f (−9.9 ppm) and g, g'' (−18.2 ppm). The element g' is excluded because of the absence of an absorption at 12 ppm due to an Si(CH$_3$)$_3$ group. However, it is possible that further silanization was achieved by a dialkoxydimethylsilane, which results in a polylayer with each silicon atom at the surface attached to two organic groups. As described above for the ^{13}C resonance of the SiCH$_3$ group, no shift difference between a SiCH$_3$ group and a SiCH$_2$R moiety is found in the ^{29}Si data. The coalescence of the signal should also be true for methylalkyldialkoxysilanes.

In the ^{13}C CP–MAS NMR spectra of commercial RP materials, we found two additional resonances at 50 and about 44 ppm. Because methoxy groups in silanes absorb at about 49 ppm (Table III), we assign the resonance at 50 ppm to Si–OCH$_3$ groups which could be derived from the starting silane. They also could have been generated by slow hydrolysis during storage and by adsorption of methanol used in the washing procedure. We conclude that the resonance at 44 ppm is the result of an adsorption of methanol through hydrogen bonds (Fig. 11). In the silica gel derivatives which we have prepared by modification with a monofunctional silane we detect also

TABLE IV

^{13}C CP–MAS NMR DATA FOR COMMERCIAL RP-SILICA GELS

A = Structural elements shown in Fig. 2.

$$X = -OH, \ -O-\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}-O-, \ -O-\overset{\displaystyle O}{\underset{\displaystyle O}{Si}}-CH_2-, \ -OR . \ \textcircled{Si} \equiv SiO_2 \ \text{surface.}$$

Silica gel	NMR data (ppm)	
Macherey, Nagel & Co. Nucleosil 5 C$_{18}$	$A+A'''$ $\textcircled{Si}-O-\overset{X}{\underset{X}{Si}}-\underset{12,2}{\overset{1}{CH_2}}-\underset{22,3}{\overset{2}{CH_2}}-\underset{32,0}{\overset{3}{CH_2}}-\underset{28,5}{\overset{4-15}{(CH_2)_{12}}}-\underset{32,0}{\overset{16}{CH_2}}-\underset{22,3}{\overset{17}{CH_2}}-\underset{12,2}{\overset{18}{CH_3}}$ $X = -0,1^{*}$	$(-OCH_3)$ 49,2
Spherisorb ODS 2	$A+A'''$ $\textcircled{Si}-O-\overset{X}{\underset{X}{Si}}-\underset{12,9}{\overset{1}{CH_2}}-\underset{22,6}{\overset{2}{CH_2}}-\underset{32}{\overset{3}{CH_2}}-\underset{29,9}{\overset{4-15}{(CH_2)_{12}}}-\underset{32}{\overset{16}{CH_2}}-\underset{22,6}{\overset{17}{CH_2}}-\underset{12,9}{\overset{18}{CH_3}}$ $X = 1,6^{*}$	$(-OCH_3)$ 50,5/44,3
Merck RP-18	A' $\textcircled{Si}-O-\overset{CH_3}{\underset{X}{Si}}\underset{0,7}{}-\underset{14,0}{\overset{1}{CH_2}}-\underset{22,4}{\overset{2}{CH_2}}-\underset{32,4}{\overset{3}{CH_2}}-\underset{29,7}{\overset{4-15}{(CH_2)_{12}}}-\underset{32,4}{\overset{16}{CH_2}}-\underset{22,4}{\overset{17}{CH_2}}-\underset{12,2}{\overset{18}{CH_3}}$	$(-OCH_3)$ 51,1
Macherey, Nagel & Co. Nucleosil 5 C$_8$	A''' $\textcircled{Si}-O-\overset{X}{\underset{X}{Si}}-\underset{11,9}{\overset{1}{CH_2}}-\underset{22,2}{\overset{2}{CH_2}}-\underset{31,9}{\overset{3}{CH_2}}-\underset{29,0}{\overset{4/5}{(CH_2)_2}}-\underset{31,9}{\overset{6}{CH_2}}-\underset{22,2}{\overset{7}{CH_2}}-\underset{11,9}{\overset{8}{CH_3}}$	$(-OCH_3)$ 50,1/44,0

* Absorption due to trimethylsilyl groups.

two signals due to OCH$_3$ groups. A possible explanation of the peak at 50 ppm is an equilibrium reaction of free silanol groups with methanol:

$$Si–OH + CH_3OH \rightleftharpoons Si–OCH_3 + H_2O$$
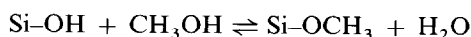
Our results are confirmed by the finding that both peaks disappear on prolonged heating of the silica gel phase above 120°C under high vacuum. Thus the assignment given by Leyden et al.[16] for silica gel silanized with chloromethylphenyltrimethoxy-silane, assigning the absorptions at 43 and 50 ppm to the benzylic carbon atom, must be incorrect. Using the above assignments of NMR spectra, changes of chemically bondes phases, until now only detectable by the chromatographic behaviour, can be understood and improvements achieved.

It can be expected that in the future solid-state NMR spectroscopy will also give information on the molecular mechanism of the interaction between stationary

TABLE V

^{29}SI CP–MAS NMR DATA OF COMMERCIAL RP-SILICA GELS

Silica gel	Chemical shift value (ppm)	Assignment
Shandon ODS-Hypersil	+12.1	d
	−55.8	k + (k′) + k″
	−66.8	l′
	−100.2	b
	−109.9	a
Macherey, Nagel & Co. Nucleosil 5 C_{18}	+12.7	d
	−49.5	i
	−57.1	k + (k′) + k″
	−66.4	l′
	−100.1	b
	−110.3	a
Macherey, Nagel & Co. Nucleosil 5 C_8	−49.5	i
	−56.9	k + k″
	−66.2	l′
	−101.9	b
	−110.8	a
Merck RP-18	−9.9/−8.4	e + f
	−18.2/−17.1	g + g″
	−101.5/−100.6	b
	−110.5/−109.8	a
Merck RP-8	−7.9	e + f
	−16.0	g + g″
	−100.8	b
	−110.0	a
Spherisorb ODS 2	+12.9/9.9	d
	−25 (weak)	
	−48.2	i
	−57.1	k + (k′) + k″
	−66.4	l′
	−100	b
	−109.1	a

phases and both the mobile phases and solutes. Investigations of the conformation of the organic groups bound to the silica matrix are also possible. This certainly will contribute to the further development of columns in liquid chromatography.
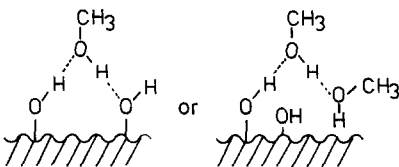

Fig. 11. Schematic representation of physisorbed methanol.

REFERENCES

1 L. Horner and F. Schumacher, *Justus Liebigs Ann. Chem.*, (1976) 633.
2 R. R. Hautala, R. B. King, E. M. Sweet, J. L. Little and A. W. Shields, *J. Organomet. Chem.*, 216 (1981) 281.
3 R. W. Murray, *Acc. Chem. Res.*, 13 (1980) 135.
4 S. L. Regen, *Angew. Chem.*, 91 (1979) 464.
5 A. V. Kiselev and V. J. Lignin, *Infrared Spectra of Surface Compounds*, Wiley-Interscience, New York, 1975.
6 K. K. Unger, *Porous Silica*, Elsevier, Amsterdam, 1979.
7 M. L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Marcel Dekker, New York, 1967.
8 H. Ishida and J. L. Koenig, *J. Colloid Interface Sci.*, 64 (1978) 555.
9 J. Schaefer and E. O. Stejskal, *Top. Carbon NMR Spectrosc.*, 3 (1979) 283.
10 J. Schaefer and E. O. Stejskal, *J. Amer. Chem. Soc.*, 98 (1976) 1031.
11 S. R. Hartmann and E. L. Hahn, *Phys. Rev.*, 128 (1962) 2042.
12 A. Pines, M. G. Gibby and J. S. Waugh, *J. Chem. Phys.*, 59 (1973) 569.
13 H. L. Retkofsky and D. L. van der Hart, *Fuel*, 57 (1978) 421.
14 E. O. Stejskal, J. Schaefer, M. D. Sefcik, G. S. Jacob and R. A. McKay, *Pure Appl. Chem.*, 54 (1982) 461.
15 W. H. Dawson, S. W. Kaiser, P. D. Ellis and R. R. Inners, *J. Amer. Chem. Soc.*, 103 (1981) 6780.
16 D. E. Leyden, D. S. Kendall and T. G. Waddell, *Anal. Chim. Acta*, 126 (1981) 207.
17 C.-H. Chiang, N. Liu and J. L. Koenig, *J. Colloid Interface Sci.*, 86 (1982) 26.
18 G. Engelhardt, H. Jancke, E. Lippmaa and A. Samoson, *J. Organomet. Chem.*, 210 (1981) 295.
19 G. A. Maciel and D. W. Sindorf, *J. Amer. Chem. Soc.*, 102 (1980) 7606.
20 D. W. Sindorf and G. E. Maciel, *J. Amer. Chem. Soc.*, 103 (1981) 4263.
21 E. Bayer, K. Albert, M. Nieder, E. Grom, G. Wolff and M. Rindlisbacher, *Anal. Chem.*, 54 (1982) 1747.
22 G. E. Maciel, D. W. Sindorf and V. J. Bartuska, *J. Chromatogr.*, 205 (1981) 438.
23 J. Reiners, *Dissertation*, Universität Tübingen, Tübingen, 1982.
24 M. Nieder, *Dissertation*, Universität Tübingen, Tübingen, 1982.
25 C. J. Little, A. D. Dale and J. A. Whatley, *J. Chromatogr.*, 171 (1979) 431.
26 K. K. Unger, N. Becker and P. Roumeliotis, *J. Chromatogr.*, 125 (1978) 115.
27 H. C. Marsmann, *Z. Naturforsch. B*, 29 (1974) 495.