Article

Surface Characterization of Some Novel Bonded Phase Packing Materials for HPLC Columns Using MAS-NMR Spectroscopy

Jude Abia

Department of Chemistry, Northeastern State University, Broken Arrow, OK 74014, USA;
E-Mail: abia@nsuok.edu; Tel.: +1-918-449-6477; Fax: +1-918-449-6473

Abstract: Information on the surface properties of three novel chemically bonded phase packing materials for High performance liquid chromatography (HPLC) were obtained using spectra obtained by solid state cross-polarization (CP) magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopic experiments for the ^{29}Si, and ^{13}C nuclei. These packing materials were: Cogent bidentate C_{18} bonded to type-C silica, hybrid packing materials XTerra MS C_{18}, and XBridge Prep. C_{18}. The spectra obtained using cross-polarization magic angle spinning (CP-MAS) on the Cogent bidentate C_{18} bonded to type-C silica show the surface to be densely populated with hydride groups (Si-H), with a relative surface coverage exceeding 80%. The hybrid packing materials XTerra and XBridge gave spectra that reveal the silicon atoms to be bonded to organic moieties embedded in the molecular structure of these materials with over 90% of the alkyl silicon atoms found within the completely condensed silicon environments. The hydrolytic stability of these materials were investigated in acidic aqueous solutions at pHs of 7.0 and 3.0, and it was found that while the samples of XTerra and XBridge were not affected by hydrolysis at this pH range, the sample of Cogent lost a significant proportion of its Si-H groups after five days of treatment in acidic aqueous solution.

Keywords: surface characterization; MAS-NMR; packing materials; HPLC

1. Introduction

High performance liquid chromatography (HPLC) remains one of the most widely used separation methods in chemical analysis. It provides analysts with the qualitative and quantitative information that

they need on the composition of a wide variety of samples [1–5]. It is estimated that 80% of all separations made in pharmaceutical, biomedical, and, environmental analyses are performed with HPLC [6]. This explains why there is a constant interest in the preparation and evaluation of new packing materials for HPLC columns, as well as in the optimization of chromatographic systems [7].

Recent innovations in column technology are geared toward providing scientists the ability to extend the limits of HPLC technology for higher speed, higher column efficiency, more symmetrical peak shapes, and column stability in a wider pH range. Much work is being invested in extending the analytical capability of reverse-phase high performance liquid chromatography (RPLC) and these efforts are concentrated on the preparation of fine particles of new silica-based, chemically bonded packing materials (CBPs). Alkyl bonded ligands like C_2, C_8, and C_{18} are the most widely used to prepare packing materials for RPLC, whereas specific applications may require CBP with polar functional groups (e.g., –CN, –NH_2, –NO_2, –OH) or some other chiral moiety. Porous silica and hybrid organic/silica materials are commonly used in the preparation of CBPs. The physico-chemical characteristics of these particles are known. The concentration of silanol groups, the type and structure of the matrix, and its porosity can strongly influence the density and structure of CBPs. Therefore, recognition of such surface properties is helpful in optimizing separation processes based on RP-HPLC. Polar, acidic silanol (Si-OH) functional groups are found on the surface of all silica-based stationary phases. Even after a surface has been derivatized, numerous residual silanols remain on the unbonded regions of the surface, in part because silica particles have a complex structure of many small pores (sizes range from 90–135 Å), and bulky reagents like octadecylsilane have a limited ability to reach their surface because some silanol groups are hindered by previously bonded ligands or have a low reactivity. This is undesirable if it contributes to unwanted interactions like the electrostatic attraction of analytes by these Si-OH groups. Ion-exchange interactions of basic compounds with acidic residual silanols can also cause tailing of their peaks [8].

Limiting such shortcomings was the rationale for the development of Cogent bidentate C_{18} type-C silica, whose surface is populated with silicon-hydride groups (Si-H), rather than with Si-OH groups [9]. The basic chemical reaction used in the fabrication process for silica hydride involves the utilization of a silanization reaction that produces a surface populated with silicon-hydride groups (Si-H). The silanized silica can then undergo hydrosilation as further modification to produce stationary phases of desired properties (e.g., hydrophobic, hydrophilic, chiral, *etc.*). Some unique and helpful chromatographic qualities are due to this feature of the Cogent material. For example, it could be less prone to some limitations mentioned earlier associated with the presence of free silanols on the surface [9,10].

Another approach to the design of improved packing materials for HPLC columns involves redefining in a fundamental way the structure of the underlying matrix by producing organic/inorganic hybrids, which combine the positive attributes of both silica and polymers. These columns are now marketed under the commercial names of XTerra and XBridge. In the patented manufacturing process of these columns or Hybrid Particle Technology, one out of every three silanol groups is replaced with an alkyl group, a methyl group for XTerra, an ethyl bridge for XBridge. Because the entire structure of the particle backbone has a distributive hydrophobicity, the result is a rugged hybrid (inorganic/organic) particle. The process for making these hybrid materials is illustrated in Equation (1) [11].

$$(RO)_4Si + n\ (RO)_3SiR^* + (1.5\ n + 2)\ H_2O \rightarrow SiO_2(R^*SiO_{1.5})_n + (3\ n + 4)\ ROH \qquad (1)$$
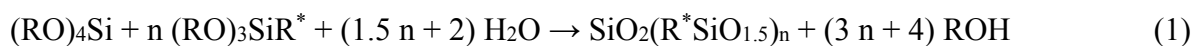
R represents an alkyl group. Two high-purity monomers are mixed. During particle formation, inorganic units (SiO_2), and organosiloxane units ($RSiO_{1.5}$) combine. A carefully controlled polymerization process creates particles having the right organic/inorganic balance. These particles can then be surface-bonded and nonpolar groups (e.g., C_{18}, C_8) are attached. Therefore, such particles combine the properties of the broad pH tolerance of polymer-based packing materials with the full range benefits of silica-based packings [11].

Surface characterization of chemically bonded stationary phases for chromatography has been performed using cross-polarization and magic-angle spinning (CP-MAS) NMR [12–25]. In usual organic solids, strong dipole-dipole interactions are predominant. For an isolated spin pair, the dipole-dipole interaction **D** depends on the magnetogyric ratios γ_I, and γ_s of the two spins I and S, the distance r between the nuclei, and the orientation of their binding vector relative to the external field, which is expressed by the angle Θ in the relationship shown in Equation 2 [26,27].

$$D \propto \gamma_I \gamma_s r^{-3} (1 - 3\cos^2 \Theta) \tag{2}$$

The interaction between the dipole can cause lines to broaden by up to several kHz. In the case of nuclei of low chemical abundance like ^{31}P or those with low natural abundance like ^{13}C and ^{29}Si in organic materials, the homonuclear dipole-dipole interactions are small as a result of the large distance between two spin pairs and so heteronuclear dipole-dipole interactions with protons are predominant. However, these heteronuclear interactions can be reduced by fast sample-spinning around the magic angle $\theta = 54.74°$ (MAS). In a CP-MAS NMR experiment, the magnetization that is detected is generated by polarization transfer from a second nuclide (most commonly ^1H). The sensitivity enhancement of the "rare spin" (e.g., ^{29}Si) due to both the polarization transfer and the shorter proton relaxation times enables faster pulse repetition rates [26,27]. Thus CP-MAS can improve the sensitivity of NMR, help determine structural connectivity, and produce information on the silicon environments within solid matrices [28–30].

The goal of this work was to characterize the surface properties of Cogent bidentate C_{18} on type-C silica, XTerra MS C_{18}, and XBridge Prep. C_{18} packing materials using solid state ^{29}Si and ^{13}C cross-polarization and magic-angle spinning (CP-MAS) NMR, and to correlate the results to some observed chromatographic behavior of these materials. Both derivatized XTerra and XBridge have trifunctional C_{18} and trimethyl endcapping.

To obtain quantitative measurements from CP-MAS spectra, it is usual for several spectra to be obtained at different contact times. A plot of peak intensity of each resonance versus contact is generated and quantitative results are deduced from this [31,32]. But Maciel *et al.* showed that quantitative results from the intensity versus contact time experiment on silica gel was similar to that obtained from integrated peak areas [31]. Hence, in this work, the relative (not to be confused with the absolute) concentrations of the different environments around silicon atoms were obtained by comparing the peak intensities of the silicon resonances.

2. Experimental Section

2.1. Materials and Sample Preparation

The packing materials used for our studies were fine white powder generously contributed from two sources: J. Pesek (McroSolv Tech Corp., Eatontown, NJ, USA) donated bare silica (spherical shaped

5.2 μm, 98 Å, thermally treated sol-gel-type-B silica; washed with acid for low metal content of <10 ppm) and the packing material Cogent bidentate C_{18} on type-C silica. The hybrid packing materials (both underivatized and derivatized) XBrigde and XTerra were gifts from U. Neue (Waters Corp., Milford, MA, USA). Figure 1 shows the surface structure of these hybrid materials. A summary of some properties of these packing materials is shown in Table 1.
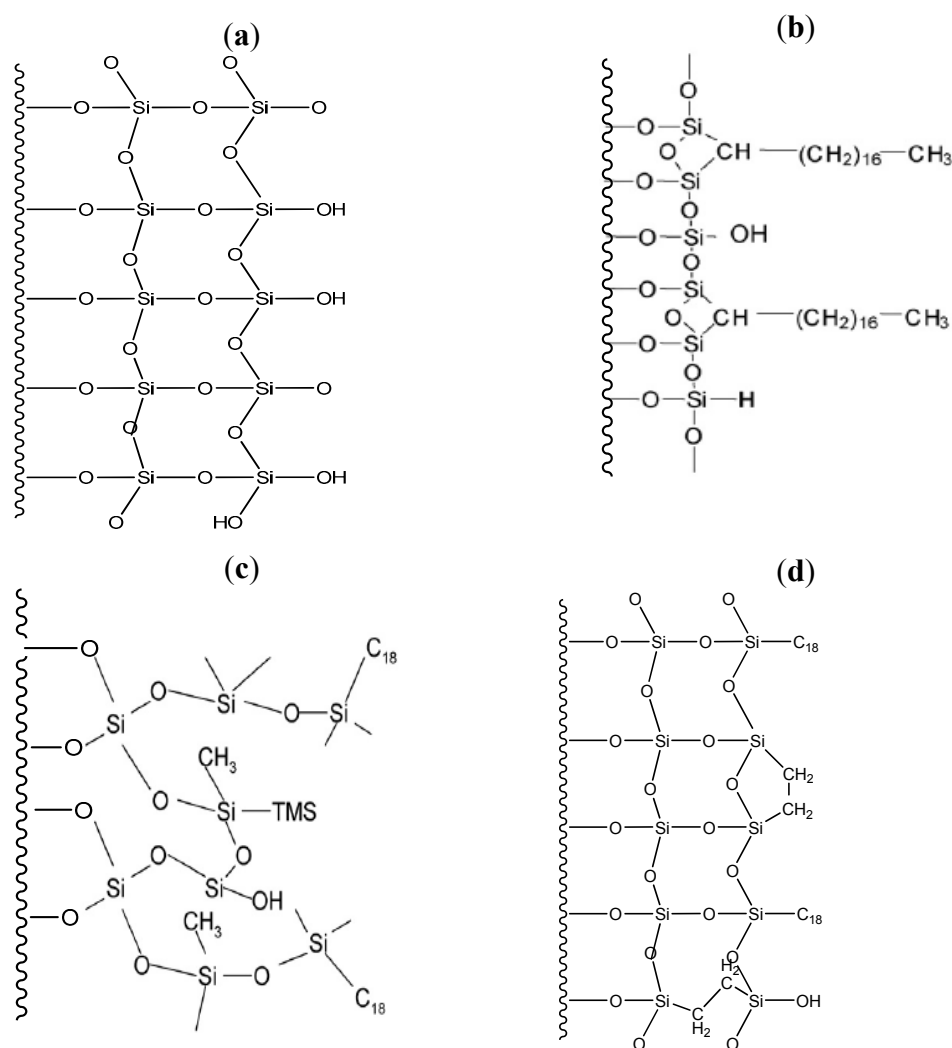
Figure 1. Representative surface chemical structure of (**a**) bare silica (**b**) cogent bidentate C_{18} (**c**) XTerra MS C_{18}; Trimethylsilane (TMS) endcapping shown (**d**) XBridge Prep C_{18}.

Table 1. Summary of characteristics of packing materials.

Property	Cogent bidentate C_{18}	XTerra	XTerra MS C_{18}	XBridge	XBridge Prep. C_{18}
Particle size (μm)	4	5	5	5	5
Pore size (Å)	100	120	120	135	135
Pore volume (mL/g)	0.92	0.64	0.64	0.70	0.70
Surface area (m²/g)	350	176	176	185	185
Carbon load (%)	16.0	n/a	15.5	n/a	18.0
Ligand density (μmol/m²)	n/a	n/a	2.40	n/a	3.10
Endcapped	No	n/a	Yes	n/a	Yes

Prior to NMR measurements, samples were tightly packed into a cylinder and placed in a special double-bearing rotor of ZrO_2 so that the cylinder is oriented at 54.74° to the magnetic field of the NMR instrument and spun.

The hydrolytic stability of the Cogent bidentate C_{18}, XTerra MS C_{18}, and XBridge prep C_{18} packing materials were examined by subjecting the materials to water under constant shaking for five days. Water at pH 7 and 1 mM HCl solution (pH 3) were used. After this, the thoroughly wet materials were dried in a vacuum oven at 40 °C for 48 h, allowed to cool, then ^{29}Si CP-MAS spectra were obtained.

2.2. Instruments and Experiments

Cross-polarization, magic-angle spinning (CP-MAS) NMR spectra were recorded with a solid state Varian INOVA 400 MHz wide-bore magnet spectrometer (Varian, Inc. Palo Alto, CA, USA) that is equipped with a chemagnetic 5 mm MAS probe and spinning at 5 kHz. The conditions used for acquiring the spectra were: a 2 ms contact time, a pulse width of 7 µs, and a delay time of 3 s. To acquire the ^{13}C CP-MAS spectra, 512 scans were used while for ^{29}Si CP-MAS spectra, 1024 scans were obtained. All spectral shifts were recorded relative to tetramethylsilane. For the ^{29}Si CP-MAS experiments, the Hartmann-Hahn match was set using an external standard hexamethylcyclotrisiloxane (^{29}Si CP-MAS NMR, δ −9.62), with a sample spinning rate of 5 kHz. On the other hand, adamantane (^{13}C CP-MAS NMR, δ 38.55) was used as the external standard for the chemical shift referencing for the ^{13}C CP-MAS experiments, with a sample spinning rate at 4.5 kHz.

A Gaussian apodization function was used to increase the signal to noise ratio for the spectra, which resulted in a band broadening of no more than 0.3 ppm [33]. When necessary, the relative concentrations of the different environments around silicon could be obtained using spectral deconvolution (using Mestrenova software) by comparison of the relative intensities of the different silicon resonances.

3. Results and Discussion

3.1. Surface Characterization of the Cogent Bidentate C_{18} on Type-C Silica

To better understand the extent of surface coverage by Si-H groups on the derivatized type-C silica, it was necessary first to record the ^{29}Si CP-MAS spectrum of an underivatized bare silica material to allow its relative comparison with that of a derivatized type-C silica. The spectrum obtained for bare silica is shown in Figure 2. Three tetrafunctional silyl groups (Q^2, Q^3, and Q^4) can be identified [29,31,34]. As expected, the bare silica surface is largely dominated by the mono-silanol groups (Q^3).

Figure 3 shows the Cogent bidentate C_{18} on type-C silica sample along with the peak identities as well as their percentage distributions. As seen in Figure 3, five resonances could be identified in this spectrum. When compared to the spectrum for the bare silica sample, some similarities are observed. The Q^n sites for the Cogent bidentate C_{18} on type-C silica have the same chemical shifts as those for the bare silica and should be similarly identified. The existence of the peak at −65.47 ppm is evidence of the presence on the surface of another bonded moiety that is attached directly to the surface by a stable Si-C bond. One example of such moieties could be groups bonded to two close-by surface silicon atoms, similar to the products that are formed when an alkyne is used in the hydrosilation reaction [9]. The

versatility that comes from attaching organic moieties to the surface Si-H groups leads to the possibility of producing such a stationary phase that may not be feasible by other methods.
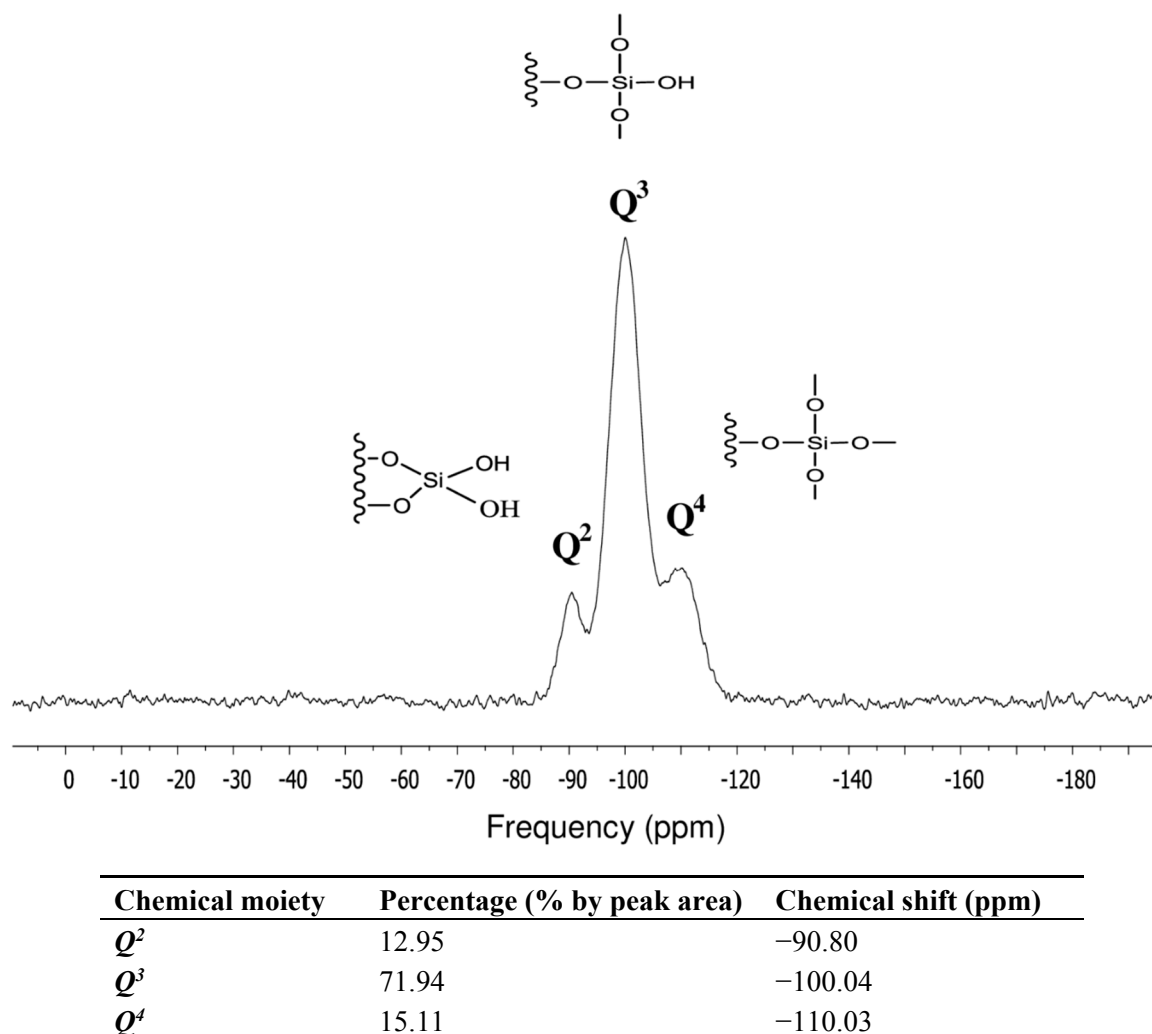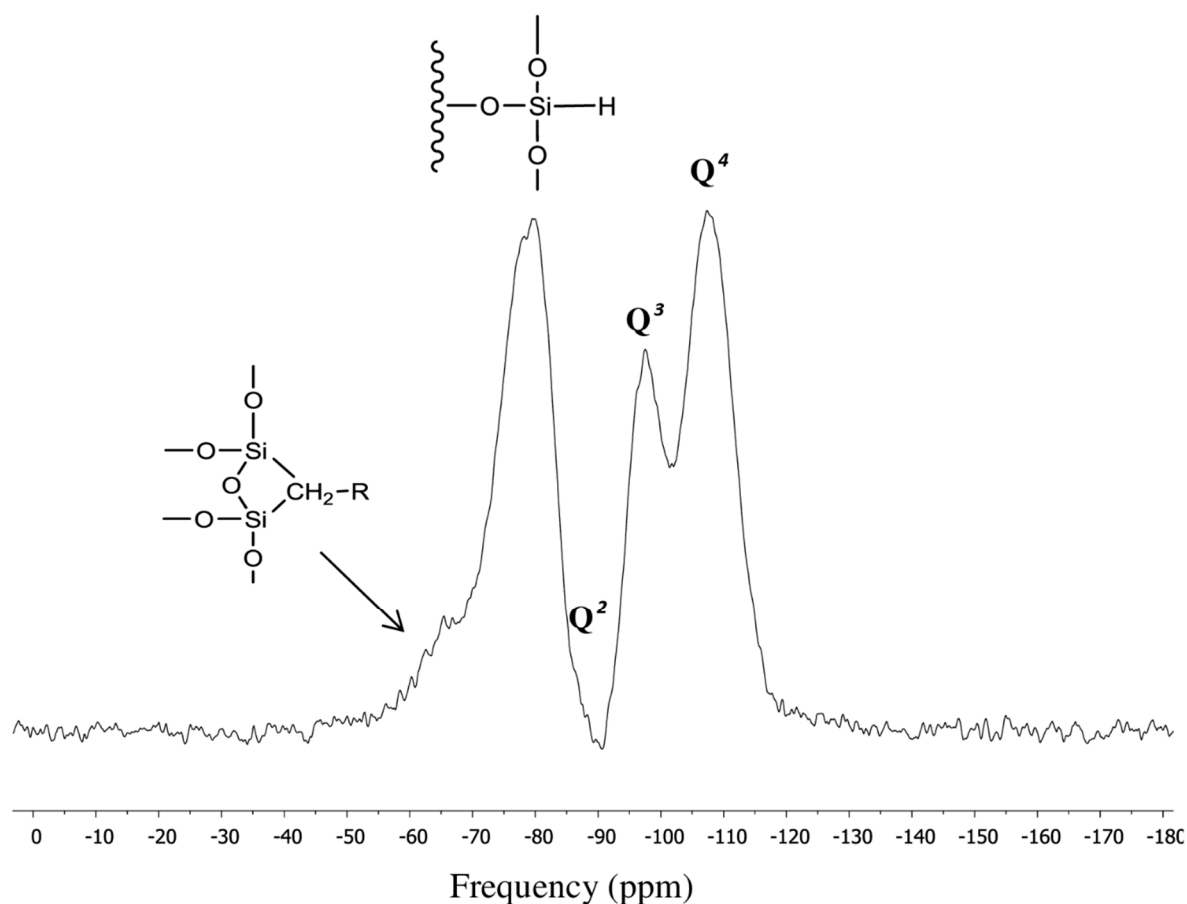

Chemical moiety	Percentage (% by peak area)	Chemical shift (ppm)
Q^2	12.95	−90.80
Q^3	71.94	−100.04
Q^4	15.11	−110.03

Figure 2. [29]Si CP-MAS spectrum of bare silica.

Another important observation is the dominance of the peak at −80.72 ppm. This peak is attributed to the Si-H moiety. The peak intensity corresponds to the substitution of about 80% of the original S-OH groups on the bare silica by Si-H groups. This result agrees well with the earlier publication of Pesek *et al.* [9] who reported that the surface of the Cogent bidentate C_{18} on type-C silica adsorbent is predominantly populated with Si-H groups instead of the Si-OH groups that dominate the surface of ordinary silica. The shoulder at −89.90 ppm corresponding to a silicon atom attached to two hydroxyl groups (Q^2 site) has a drastically reduced intensity for the Cogent bidentate type-C silica. This is an indication of the effectiveness of the substitution of silanol with silicon hydride groups in the production of this adsorbent.

However, it should be mentioned that, as determined by the [29]Si CP-MAS experiment (see Figure 3), a significant surface density of silanol groups (Q^2 and Q^3 sites) still persists on the surface of the Cogent bidentate C_{18} type-C silica. That is what prevents such a surface from being inactive. This observation is consistent with earlier findings of Gritti *et al.* [35] who showed that the retention of basic compounds

is an order of magnitude larger on Cogent than on the hybrid adsorbent (XTerra) and that peak tailings on Cogent are stronger than on XTerra. A reason that was postulated by Gritti *et al.* for this behavior of Cogent was the possible instability of the Si-H bond, as silanol groups may rapidly form once the Cogent packing is in contact with aqueous mobile phases (due to fast hydrolysis of the Si-H bonds). Solid state NMR studies to test this latter suggestion are found in Section 3.4.
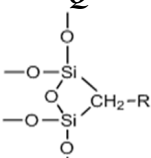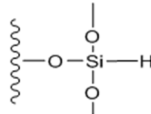

Chemical moiety	Percentage (% by peak area)	Chemical shift (ppm)
Q^2	2.84	−89.90
Q^3	10.90	−99.55
Q^4	36.99	−110.00
(bidentate CH_2-R structure)	2.80	−65.47
(O-Si-H structure)	46.47	−80.72

Figure 3. ^{29}Si CP-MAS spectrum of Cogent bidentate C_{18} on type-C silica.

3.2. Surface Characterization of the XTerra Packing Material

The simplified molecular structure of the XTerra shown in Figure 1 will help in understanding the different Si sites expected to be represented in the CP-MAS spectra. For underivatized XTerra, four silicon sites are observed in the ^{29}Si CP-MAS spectrum shown in Figure 4.
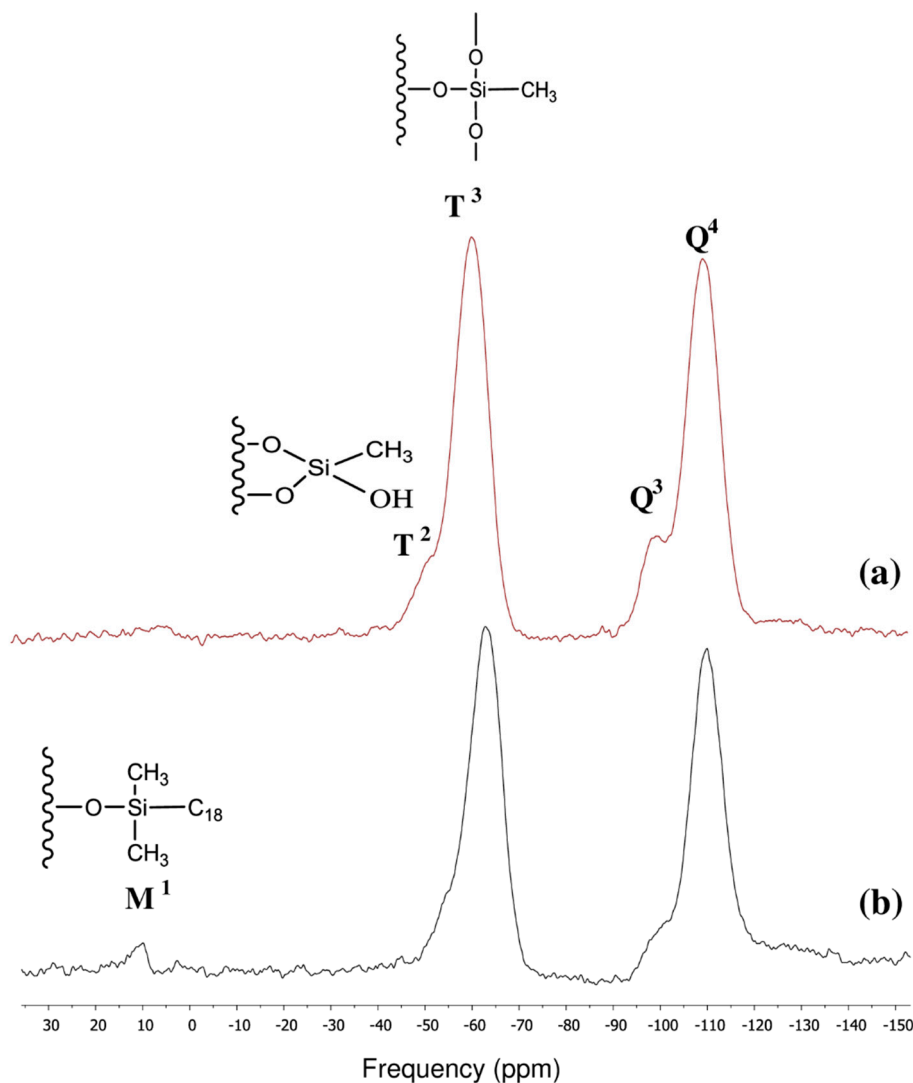

Figure 4. ^{29}Si CP-MAS spectrum of (**a**) underivatized Xterra and (**b**) XTerra MS C$_{18}$.

The chemical shift at −62.56 ppm is the trifunctional silicon and is attributed to a T^3 site which is a silicon atom attached to a carbon atom ([CSi(OSi)$_3$]), while the shoulder at −53.45 ppm is attributed to the T^2 silicon site ([CSi(OH)(OSi)$_2$]). The Q^n silicon sites can be identified as well. The peak that has a −110.00 ppm shift is that of the siloxane group (Q^4), while the small peak at −99.93 ppm corresponds to the Q^3 site [32,37]. By making relative comparisons between the T^2 and T^3 sites, it was determined that greater than 90% of the methyl silicon atoms are within the completely condensed T^3 environments.

For XTerra MS C$_{18}$, the peak identities are the same for the silicon sites Q^4, Q^3, T^3, and T^2 as they are for the underivatized XTerra. A notable addition for the XTerra MS C$_{18}$ is the M^1 environment (peak at +11.27 ppm). This is expected because these hybrid packing materials have trimethyl endcapped units. As can be expected, the relative intensity for the corresponding silanol peak (Q^3) is also greatly

diminished upon derivatization. The relative amount of Si-OH groups on the surface of the XTerra MS C_{18} is estimated to be less than 5%. Therefore, a really great majority of silicon atoms do not bear the silanol groups, which is consistent with earlier published chromatographic results showing that the retention of basic compounds is at least an order of magnitude smaller on XTerra MS C_{18} than on Cogent or other conventional material prepared by derivatizing high-purity B-type silica particles with monofunctional silanes [35].

To corroborate that the molecular structures of these hybrid packing materials do contain both organic and silica units, ^{13}C CP-MAS spectrum was obtained for XTerra MS C_{18} (see Figure 5 for the ^{13}C CP-MAS spectra and peak assignments). The bundle of peaks from +16 to +36 ppm is typical of the presence of the C_{18} ligands with the predominant peak at 32.33 ppm corresponding to the main $-CH_2$ chain [32]. The carbons of the endcapped trimethylsilane also show up at -0.36 ppm.
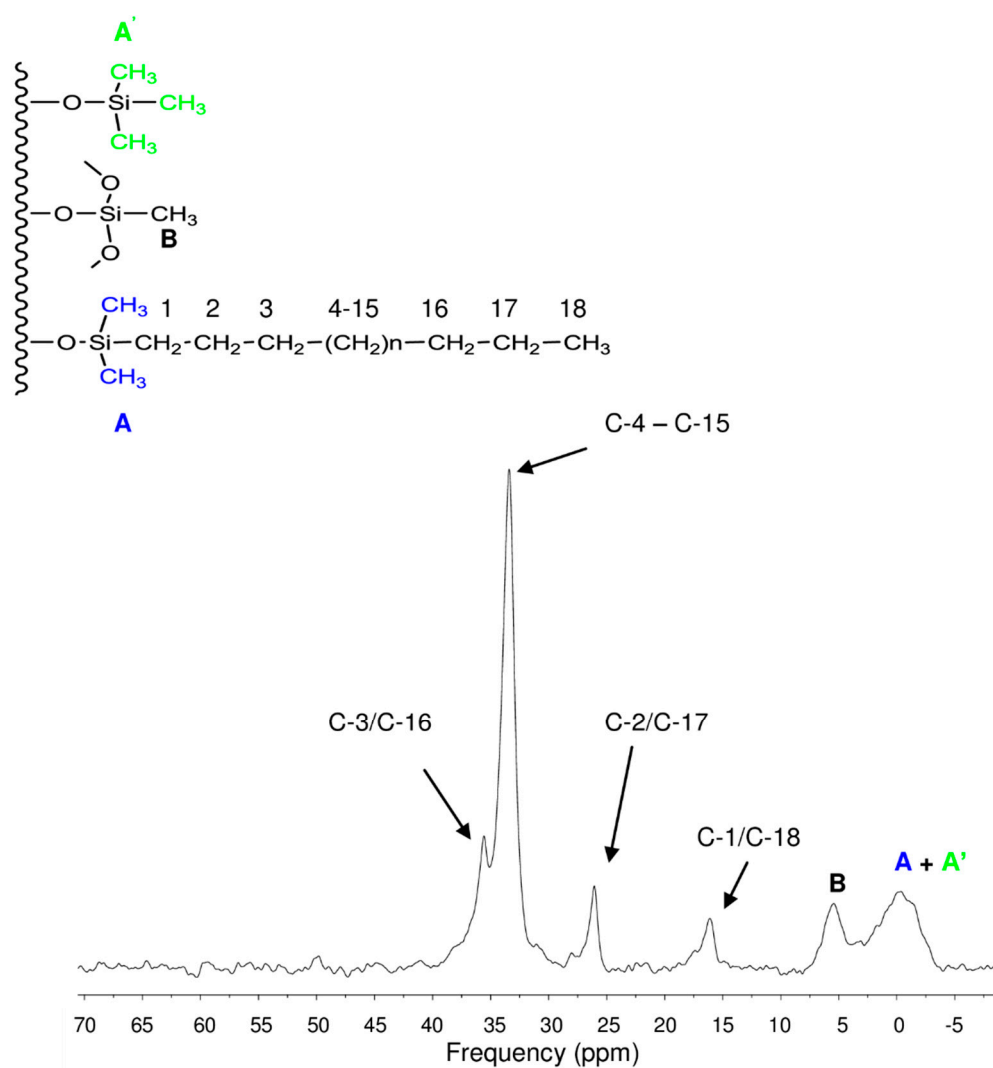

Figure 5. ^{13}C CP-MAS spectra and peak assignments for (**a**) underivatized XTerra and (**b**) XTerra MS C_{18}.

3.3. Surface Characterization of the XBridge Packing Material

The [29]Si CPMAS spectra acquired for the XBridge hybrid materials are shown in Figure 6. The spectrum for the underivatized XBridge (Figure 6a) shows two main peaks. The peak at −62.09 ppm (T^3) is attributed to silicon atoms attached to carbon atoms while the one at −110.00 ppm (Q^4) is that of a siloxane [32]. This also is evidence that the molecular structure of these hybrid packing materials do contain both organic and silica units. The small peak at −100.05 ppm (Q^3) is attributed to a silanol group, while the shoulder at −53.16 ppm corresponds to the T^2 environment [31]. Similar to the XTerra, by making relative comparisons between the T^2 and T^3 sites, it was determined that the greater majority of ethyl bridged silicon atoms (>90%) are also within the completely condensed T^3 environments.
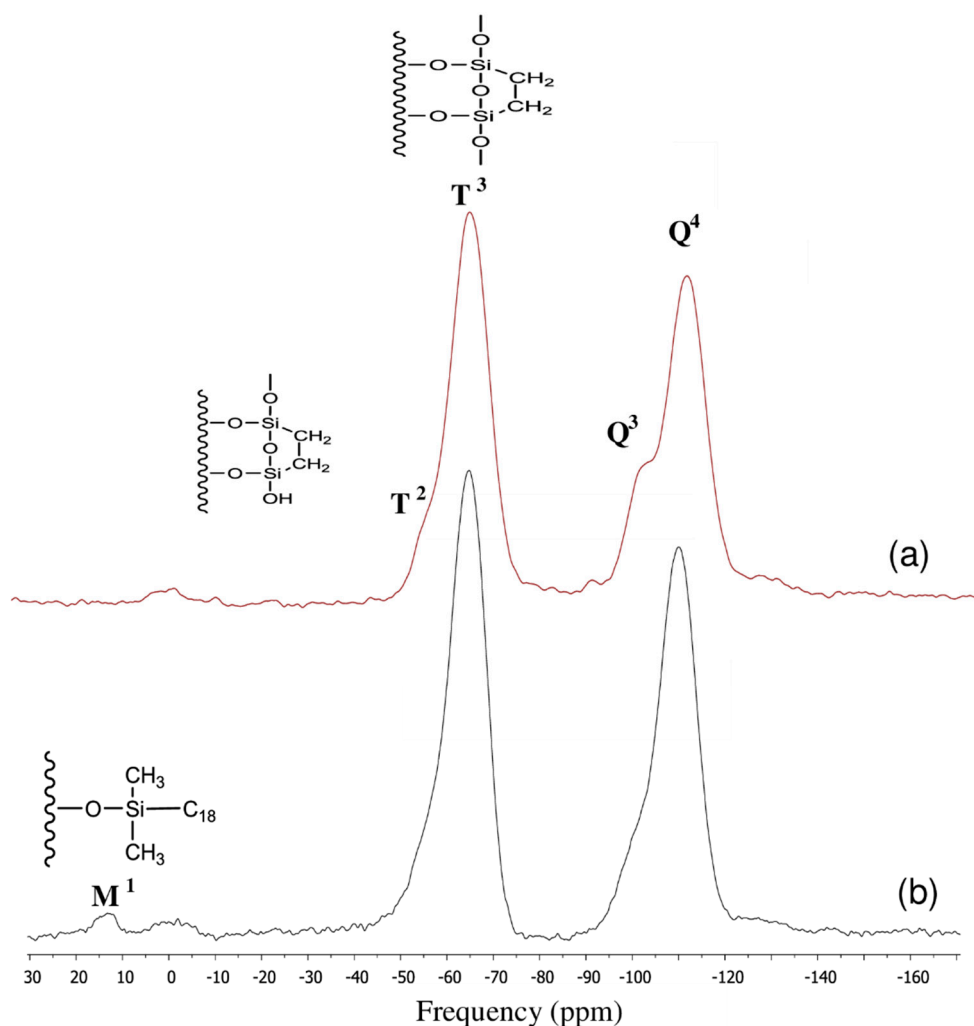

Figure 6. [29]Si CP-MAS spectra for (**a**) underivatized XBridge (**b**) XBridge prep C_{18}.

For XBridge Prep C_{18} (see Figure 6b), the identities of the peaks Q^4, Q^3, T^3, and T^2 remain unchanged relative to the underivatized XBridge because these different silicon sites are the same. Noteworthy, however, is the presence of the M^1 environment at resonance of +12.07 ppm. The peak intensity for the corresponding silanol peak (Q^3) is greatly diminished as is expected upon derivatization.

3.4. Hydrolytic Stability of Packing Materials in Aqueous Conditions

The incorporation of organic moieties in the silica matrix, which is achieved in XTerra and XBridge materials, reduces the silanol activity. Earlier experimental results showed that this was more successful in reducing the peak tailing of basic compounds than in the case (Cogent bidentate C_{18}) of chemical surface protection and elimination of most silanol groups [35]. The stability of the Si-H bond was questioned, in that silanol groups may rapidly form once the Cogent packing is in contact with aqueous mobile phases, due to the fast hydrolysis of the Si-H bonds. If this is the true, then upon the hydrolytic treatment of the Cogent C_{18}, a reduction in the intensity for the Si-H moiety can be expected in the ^{29}Si CP-MAS spectrum.

For the treated Cogent bidentate C_{18} packing material, some reduction in the peak intensity is observed for the peak corresponding to the Si-H moiety (see Figure 7). Table 2 lists all the peak assignments as well as their relative percentage by area. As can be seen in Table 4, this reduction is more important for the sample that had undergone the hydrolytic treatment under more acidic conditions. Granted, we do not see that many silanols on the dry powder, but earlier chromatographic evidence point to some increased silanol activity on packing Cogent C_{18} material [35]. This is no surprise since the Si-H sites are known to have high affinity for water adsorption [37] Therefore, the hydrolytic instability of the Si-H bond is the point of reconciliation. Because the Si-H bond is not very hydrolytically stable, it gets hydrolyzed in the presence of water, especially under acid conditions.
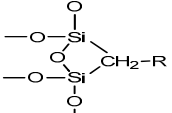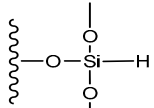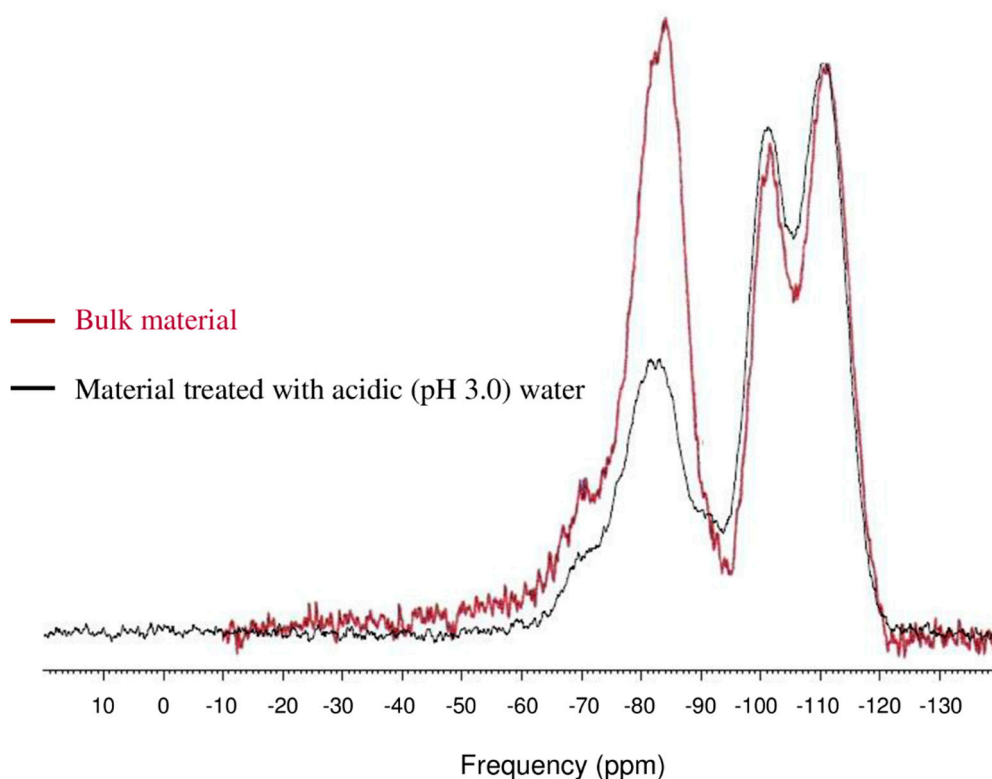

Figure 7. ^{29}Si CP-MAS spectra of bulk Cogent bidentate C_{18} on type-C silica and sample treated for five days with acidic water at pH 3.0.

Table 2. Effect of hydrolysis on the percentage distribution of the different peaks in the NMR spectra of Cogent bidentate C_{18}.

Chemical moiety	Percentage (% by peak area)		
	Untreated bulk material	Water (pH 7.0) treatment	Water (pH 3.0) treatment
Q^2	2.84	2.84	4.88
Q^3	10.90	12.90	16.59
Q^4	36.99	37.70	40.98
	2.80	2.79	3.89
	46.47	43.77	33.66

4. Conclusions

The development of Cogent type-C silica and the hybrid packing materials XTerra and XBridge are welcomed additions toward the advances made in column technology. Using solid-state ^{29}Si CP-MAS NMR spectroscopy, the degree of surface substitution of Si-OH to Si-H for the Cogent type-C packing material was made. This resultant Si-H coverage is high (~80%) for the bulk material and correlates well with what was stated earlier by Pesek *et al.* [9]. However, a significant surface density of Si-OH groups persists and this density increases when the material is treated with acidic water. This means that the Si-H bond is hydrolytically unstable and can become hydrolyzed especially in acidic water to form Si-OH groups. When this happens, the surface is no longer inactive toward undesirable retention cause by Si-OH groups [35,37].

Also, the results from ^{29}Si CP-MAS spectra obtained for the hybrid packing materials XTerra and XBridge confirm that the silicon atoms in the structure of these adsorbents are directly bonded to carbon atoms. Relative comparisons between the T^2 and T^3 sites show that greater than 90% of the alkyl silicon atoms are within the completely condensed T^3 environments. The relative amount of Si-OH groups on the surface of the XTerra MS C_{18} and XBridge prep C_{18} is estimated to be ~2%. Therefore, almost all of the silicon atoms are not silanol groups. This means that undesirable retention of compounds by the residual silanol groups is much less for the XTerra MS C_{18} and XBridge prep C_{18} than for the Cogent or another conventional material prepared by derivatizing high-purity B-type silica particles with monofunctional silanes [35].

Conflicts of Interest

The author declares no conflict of interest.

References

1. Poole, C.F.; Poole, S.K. *Chromatography Today*; Elsevier: Amsterdam, The Netherlands, 1991; pp. 649–743.
2. Pietrzyk, D.J.; Brown, P.R.; Hartwick, R.A. *High Performance Liquid Chromatography*; Wiley: New York, NY, USA, 1998.
3. Snyder, L.R.; Kirkland, J.J. *Introduction to Modern Liquid Chromatography*, 2nd ed.; Wiley: New York, NY, USA, 1977.
4. Sander, L.C.; Wise, S.A. Recent advances in bonded phases for liquid chromatography. *Crit. Rev. Anal. Chem.* **1987**, *18*, 299–415.
5. Nawrocki, J.; Buszewski, B. Influence of silica surface chemistry and structure on the properties, structure and coverage of alkyl-bonded phases for high-performance liquid chromatography. *J. Chromatogr. A* **1988**, *449*, 1–24.
6. Gerber, F.; Krummen, M.; Potgeter, H.; Roth, A.; Siffrin, C.; Spoendlin, C. Practical aspects of fast reversed-phase high-performance liquid chromatography using 3μm particle packed columns and monolithic columns in pharmaceutical development and production working under current good manufacturing practice. *J. Chromatogr. A* **2014**, *2*, 127–133.
7. Popp, M.; Sulyok, M.; Rosenberg, E. Chromatographic characterisation of a novel type of monolithic methylsilsesquioxane-based HPLC column. *J. Sep. Sci.* **2007**, *30*, 2888–2899.
8. Buszewski, B.; Jezierska, M.; Wełniak, M.; Berek, D. Survey and trends in the preparation of chemically bonded silica phases for liquid chromatographic analysis. *J. High Res. Chromatogr.* **1998**, *21*, 267–281.
9. Pesek, J.J.; Matyska, M.T. Hydride-Based Separation Materials for High Performance Liquid Chromatography and Open Tubular Capillary Electrochromatography. *Chin. J. Chromatogr.* **2005**, *23*, 595–608.
10. Bocian, S.; Buszewski, B. Residual silanols at reversed-phase silica in HPLC—A contribution for a better understanding. *J. Sep. Sci.* **2012**, *35*, 1191–1200.
11. Unger, K.K.; Becker, N.; Roumeliotis, P. Recent developments in the evaluation of chemically bonded silica packings for liquid chromatography. *J. Chromatogr. A* **1976**, *125*, 115–127.
12. Khalid, A.M.; Thakur, M.M; Thompson, W.L.; Cao, C.; Schultz, W.J. Proton MAS NMR Analysis of Phenyl Silane Functionalized Silica Nanoparticles. *NMR Spectrosc. Polym.* **2011**, *30*, 495–508.
13. Prado, A.G.; Moura, A.O.; Nunes, A.R. Nanosized Silica Modified with Carboxylic Acid as Support for Controlled Release of Herbicides *J. Agric. Food Chem.* **2011**, *59*, 8847–8852.
14. Albert, K.; Bayer, E.J. Characterization of bonded phases by solid-state NMR spectroscopy. *J. Chromatogr. A* **1991**, *544*, 345–370.
15. Albert, K.; Brindle, R.; Schmid, J.; Buszewsky, R.; Bayer, E. CP/MAS NMR investigations of silica gel surfaces modified with aminopropylsilane. *Chromatographia* **1994**, *38*, 283–290.

16. Pesek, J.J.; Matyska, M.T.; Soczewinski, E.; Christensen, P. Spectroscopic Studies of Butylphenyl, Mono-ol and Perfluorinated Bonded Phases. *Chromatographia* **1994**, *39*, 520–528.

17. Pesek, J.J.; Matyska, M.T. Synthesis and Spectroscopic Characterization of a True Diol Bonded Phase. *J. Chromatogr. A* **1994**, *687*, 33–34.

18. Pesek, J.J.; Matyska, M.T.; Williamsen, E.J.; Tam, R. Variable-Temperature Solid-State NMR Studies of Bonded Liquid Crystal Stationary Phases for HPLC. *Chromatographia* **1995**, *41*, 301–310.

19. Legrand, A.P. *The Surface Properties of Silicas*, 1st ed.; Wiley: Chichester, UK, 1998.

20. Maciel, G.; Bronnimann, C.; Hawkins, B. *Advances in Magnetic Resonance: The Waugh Symposium*; Warren, W.S., Ed.; Academic Press: San Diego, CA, USA, 1990; Volume 14, p. 125.

21. Chuang, I.S.; Kinney, D.R.; Bronnimann, C.E.; Zeigler, R.C.; Maciel, G.E. Effects of ^{1}H-^{1}H spin exchange in the 29Si CP-MAS NMR spectra of the silica surface. *J. Phys. Chem.* **1992**, *96*, 4027–4034.

22. Maciel, G.; Ellis, P. *NMR Techniques in Catalysis*; Bell, A.T., Pines, A., Eds.; Dekker: New York, NY, USA, 1994.

23. Chuang, I.; Maciel, G. Probing Hydrogen Bonding and the Local Environment of Silanols on Silica Surfaces via Nuclear Spin Cross Polarization Dynamics. *J. Am. Chem. Soc.* **1996**, *118*, 401–406.

24. Haukka S.; Lakornaa, E.; Root, A. An IR and NMR study of the chemisorption of titanium tetrachloride on silica. *J. Phys. Chem.* **1993**, *97*, 5085–5094.

25. Valtier, M.; Drujon, X.; Wilhelm, M.; Spiess, H. Quantitative Characterization of the Inner Structure of Core-Shell Latex Particles by ^{1}H Solid-State NMR. *Macromol. Chem. Phys.* **2001**, *202*, 1262–1272.

26. Engelhardt, G.; Michel, D. *High Resolution Solid-State NMR of Silicates and Zeolites*; Wiley: New York, NY, USA, 1987.

27. Reimer, J.A.; Vaughan, R.W.; Knights, J.C. Proton magnetic resonance spectra of plasma-deposited amorphous Si:H films. *Phys. Rev. Lett.* **1980**, *44*, 193–196.

28. Pines, A.; Gibby, M.; Waugh, J. Proton enhanced NMR of dilute spins in solids. *J. Chem. Phys.* **1973**, *59*, 569–590.

29. Albert, K. NMR investigations of stationaryg phases. *J. Sep. Sci.* **2003**, *26*, 215–224.

30. Pfleiderer, B.; Albert, K.; Bayer, E.; Van de Ven, L. De Haan, J.; Cramers, C. A new approach to the silica gel surface: Characterization of different surface regions by silicon-29 magic angle spinning NMR relaxation parameters and consequences for quantification of silica gels by NMR. *J. Phys. Chem.* **1990**, *94*, 4189–419.

31. Maciel, G.E.; Sindorf, W.D. Silicon-29 NMR study of the surface of silica gel by cross polarization and magic-angle spinning. *J. Am. Chem. Soc.* **1980**, *102*, 7606–7607.

32. Wyndham, K.; O'Gara, J.; Walter, T.; Glose, K.; Lawrence, N.; Alden, B.; Izzo, G.; Hudalla, C.; Iraneta, P. Characterization and evaluation of C18 HPLC stationary phases based on ethyl-bridged hybrid organic/inorganic particles. *Anal. Chem.* **2003**, *75*, 6781–6788.

33. Challoner, R.; Harris, R.; Packer, K.; Taylor, M. Solid-state NMR studies of the high-silica zeolite Theta-1. *Zeolites* **1990**, *10*, 539–545.

34. Sindorf, W.D.; Maciel, G.E. Silicon-29 NMR study of dehydrated/rehydrated silica gel using cross polarization and magic-angle spinning. *J. Am. Chem. Soc.* **1983**, *105*, 1487–1493.

35. Gritti, F.; Perdu, C.; Guiochon, G.A. Comparison of the performance of a few packing materials designed to minimize the thermodynamic band tailing of basic compounds in reversed-phase liquid chromatography. *J. Chromatogr. A* **2008**, *1180*, 73–89.

36. Zhu, G.; Yang, Q.; Jiang, D.; Yang, J.; Zhang, L.; Li, Y.; Li, C. Synthesis of bifunctionalized mesoporous organosilica spheres for high-performance liquid chromatography. *J. Chromatogr. A* **2006**, *1103*, 257–264.

37. Bociana, S.; Rychlickib, G.; Matyskac, M.; Pesekc, J.; Buszewski, B. Study of hydration process on silica hydride surfaces by microcalorimetry and water adsorption. *J. Colloid Interf. Sci.* **2014**, *416*, 161–166.