

Investigation on conformational order and mobility of DiamondBond-C18 and C18-alkyl modified silica gels by Fourier transform infrared and solid-state NMR spectroscopy

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Received 11 March 2005; received in revised form 28 April 2005; accepted 2 May 2005

Abstract

The effect of surface coverage and solid supports on the conformational order of alkyl chains of commercially available carbon clad zirconia based supports and synthesised C18-alkyl modified silica based supports are probed in the dry state for the first time using variable temperature Fourier transform infrared (FT-IR) and solid-state ¹³C NMR spectroscopy. From FT-IR spectroscopy, the conformational order of alkyl chains tethered to the substrates is examined by the analysis of CH₂ symmetric and anti-symmetric stretching bands. Through solid-state ¹³C NMR spectroscopy, the order is inferred from the relative intensity of the main methylene carbon resonance assigned to trans and trans-gauche conformations. It is found that molecules tethered to the graphite layer experience a strongly diamagnetic component of the highly anisotropic magnetic susceptibility of the graphite lattice, which reflects upfield shift in the ¹³C NMR spectra of commercially available octadecyl-modified carbon clad zirconia based column materials. The present results prove that temperature, surface coverage and solid supports have an influence on the conformational order and mobility of alkyl chains tethered to the carbon clad inorganic metal oxides.

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Keywords: *n*-Alkyl modified silica gels; Carbon clad zirconia-based supports; Conformational order; FT-IR spectroscopy; Solid-state NMR spectroscopy

1. Introduction

Zirconia based phases have been used as stationary phase materials in high-performance liquid chromatography (HPLC) for well over a decade. The development of HPLC as an efficient separation technique has been largely reliant upon the synthesis of new efficient and selective stationary phase materials. An understanding of the underlying chemical architecture and dynamics of such materials is a prerequisite for the development of new stationary phase materials.

Silica based stationary phase traditionally are used as a substrate material for HPLC due to their high mechanical strength, narrow particle size distribution, high specific

surface area, variance of pore size and well-documented chemistry of surface modification [1]. Among the different modified silica phases, the octadecyl-modified system has become more popular since the majority of organic compounds are hydrophobic enough to interact with C18 chains to some extent. Nevertheless, the silica based stationary phase materials have certain limitations such as remaining adsorptivity towards basic (amines) compounds due to silanol interactions, leading to asymmetric peaks and also lack of pH stability because the silica backbone Si–O–Si hydrolyses at pH >8, and the siloxane bond is unstable at pH <2. Use of column temperatures above 60 °C can also result in hydrolysis of the stationary phase from silane-modified silicas [2].

Titania, zirconia, alumina and magnesia provide chemically stable alternatives to silica as chromatographic stationary phase materials. These supports are superior to

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silica with respect to mechanical stability and chemical inertness within a pH range of 1–14 [3]. Unger et al. have compared the chromatographic performance of zirconia, silica, alumina and titania in the normal phase HPLC mode and showed that zirconia is superior in the separation of basic compounds [1,4]. Nawrocki et al. studied the physical and chemical properties of microporous zirconia that exhibited excellent properties as a stationary phase material [3]. Zirconia based chromatographic phases have the potential to overcome the drawbacks of silica. Zirchrom and Cabot Corporation developed a novel stationary phase material by attaching C18 chains to a chemically and thermally inert carbon clad zirconia surface which has good efficiency, extreme chemical and thermal stability and a very different chromatographic selectivity compared to all silica C18 stationary phases [5,6].

Chromatographic measurements provide vital information about the properties of the bonded phase as a function of mobile phase, temperature, stationary phase support, solute hydrophobicity and polarity [7–9]. Such studies, however, provide only indirect evidence about the bonded phase morphology. On the other hand, by using techniques like FT-IR [10–12], Raman spectroscopy [13–16], atomic force microscopy [17], NMR spectroscopy [18,19] and ellipsometry [17] more direct information about the alkyl chain structure, conformation and dynamics of the chromatographic column material is accessible. In such materials, the conformational order of the alkyl chain moieties is expected to be a major source for the selectivity during chromatographic separations. Recent studies have cleared that the conformational order, chain dynamics and their concomitant effects on retention and selectivity depends on various factors such as alkyl chain lengths, surface coverage, supporting material, temperature and pressure [10–12]. Describing the alkyl chain conformational order on the molecular level is thus crucial for the understanding of such materials in their respective chromatographic applications.

FT-IR spectroscopy has been utilized for probing the conformational order of alkyl chains in quite different ranges of alkyl materials. For instance, FT-IR absorption frequencies, band intensities and band widths have been used to study the conformation, structure and chain packing in polyethylene chains [20], *n*-alkyl modified silica gels [11], self-assembled monolayers (SAMs) [12], pure hydrocarbons and biological membranes [20]. Solid-state NMR spectroscopy is an important tool for studying the alkyl chain mobility and conformational order of the stationary phases. The combination of cross polarization (CP) with magic angle spinning allows acquisition of high-resolution NMR spectra of low-abundance heteronuclei like ^{13}C and ^{29}Si in reasonable measuring times. The carbon nuclei offer a wider chemical shift range (220 ppm) than protons (12 ppm) and therefore provide a sensitive indicator of structural changes and the conformational order of immobilized ligands. In solid-state ^{13}C NMR study order is typically inferred from the relative intensity

of the main methylene carbon resonance assigned to “crystalline like” trans and “solution-like” mixture of trans and gauche conformations [18].

Very few studies about the conformational order and dynamics have been carried out on zirconia-based stationary phase materials. Since the small molecules can freely interact with both the stationary phase and the underlying substrate, the morphology of both alkyl chains behaviour and substrate need to be understood. In the present contribution, FT-IR and solid-state ^{13}C NMR investigations probing the effect of temperature, surface coverage and solid supports on the conformational order and mobility of the alkyl chains of commercially available DiamondBond-C18 systems in the dry state are presented. The results are directly compared with the data from a parallel study on octadecyl-modified silica gels and with data on related systems.

2. Experimental

2.1. DiamondBond-C18 column materials

The DiamondBond-C18 column materials were synthesized using procedures similar to those described elsewhere [21]. The level of surface coverage with C18 groups can be varied by changes in the stoichiometry of the surface modification reaction. In the present work two different DiamondBond-C18 column materials were studied, i.e.: (i) low density DiamondBond-C18 (hereafter denoted as LDZr-C18) with a surface coverage of $2.5 \mu\text{mol}/\text{m}^2$ and (ii) high density DiamondBond-C18 (hereafter denoted as HDZr-C18) with a surface coverage of $4.0 \mu\text{mol}/\text{m}^2$.

2.2. Synthesis of C18-alkyl modified silica gels

The C18-alkyl modified silica gels (hereafter denoted as Si-C18) with a surface coverage of $4.2 \mu\text{mol}/\text{m}^2$ were synthesized using the procedure as mentioned in the earlier publication [11].

2.3. Sample preparation

The samples were measured by means of the KBr pellet technique. The pellets of the samples and KBr (1/10–1/15, w/w) of 1 mm thickness were prepared under vacuum using a hydraulic press. For the solvent studies, the powdered sample was placed between two KBr windows using a $25 \mu\text{m}$ zinc spacer and about $20 \mu\text{l}$ of solvent was added. The pellets of the respective samples were placed in a brass cell equipped with an external thermocouple in close vicinity of the sample. The cell compartment was thermostated with a variable temperature unit (L.O.T. – Oriol, Langenberg, Germany) equipped with KBr windows. The same thermocouple was also used for monitoring the actual sample temperature. The temperature was regulated with an automatic temperature control unit with an accuracy of $\pm 0.5 \text{ K}$.

2.4. IR measurements

IR spectra were recorded on a Nicolet Nexus 470 FT-IR spectrometer (Nicolet, Madison, WI, USA) equipped with a DTGS detector. Typically, 256 interferograms covering a spectral range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1} were collected within a temperature range from 193 to 353 K. The recorded interferograms were apodized with a triangular function and Fourier transformed with two levels of zero filling. Correction for background absorption was done by recording the background spectrum of the empty cell (measured with twice the number of interferograms as that used for the sample). The background spectrum was automatically subtracted from the sample spectra. Data from three independent samples were acquired at all temperatures for all the samples studied. The whole series of variable temperature FT-IR spectra was measured twice for each sample. The data analysis is thus based on an average of six measurements.

The processing and analysis of the spectra for CH_2 stretching band analysis was done with OMNIC E.S.P.5.1 software. The frequencies of the CH_2 stretching vibrations were performed from the interpolated zero crossing in the first derivative spectra.

2.5. NMR measurements

The ^{13}C CP/MAS experiments were performed by using an MSL 300 NMR spectrometer (Bruker, Rheinstetten, Germany) with a 1 kW linear amplifier stage (LPPA-13010, Dressler, Stollberg, Germany) at a ^{13}C resonance frequency of 75.47 MHz. Variable temperature ^{13}C CP/MAS NMR measurements were done with cross-polarisation conditions using a commercial 4 mm MAS probehead. The sample spinning frequency was 5 kHz, whereas the proton 90° pulse length and last delay were 6.6 μs and 6 s, respectively.

3. Results and discussion

To understand the local molecular environments and structural arrangement of the carbon-clad zirconia based

DiamondBond-C18 systems and C18-alkyl modified silica gels (Fig. 1), variable temperature FT-IR as well as NMR spectroscopy are utilised, since both can be used to get complementary information of the tethered alkyl chains attached to the different metal oxides. Conformational order in the DiamondBond-C18 column material and C18-alkyl modified silica gel are assessed using FT-IR spectroscopy from the position of the CH_2 symmetric and anti-symmetric stretching bands. In principle, quantitative information about the presence and amounts of various gauche conformers (kink/gauche-trans-gauche (gtg), double gauche, and end gauche conformers) is feasible by the analysis of the wagging band intensities between 1330 and 1400 cm^{-1} . The analysis was not possible for the present DiamondBond-C18 systems due to overlapping of other peaks, which are likely due to the phenyl-graphite layer modified substrate. Therefore, only qualitative studies are performed for the present column materials. Several attempts were made in order to study the conformational order of DiamondBond-C18 systems in the presence of various mobile phases, which would be of more interest for the comparison under chromatographic conditions. In fact, it is known that the presence of a mobile phase has impact on the conformational properties of the attached alkyl chains as compared to the dry state [13]. In order to do so, the DiamondBond-C18 powdered samples were placed between two KBr windows. Then, solvent was introduced into the KBr windows to study the influence of solvents on the conformational order of alkyl chains in the DiamondBond-C18 systems. In this case, however, the spectral quality was so poor most probably due to the higher concentration of DiamondBond-C18 materials, which made the analysis of the IR spectra impossible. Several attempts to overcome this problem were not successful. Thus, the present FT-IR study only comprises experiments of dry materials.

Through ^{13}C NMR spectroscopy, the chain ordering is obtained via analysis of ^{13}C NMR spectra where trans and gauche NMR signals can be clearly distinguished [18]. The present investigation thus provides—on the basis of different ^{13}C NMR chemical shift values—qualitative information about the chain ordering of the chains attached to the solid supports.

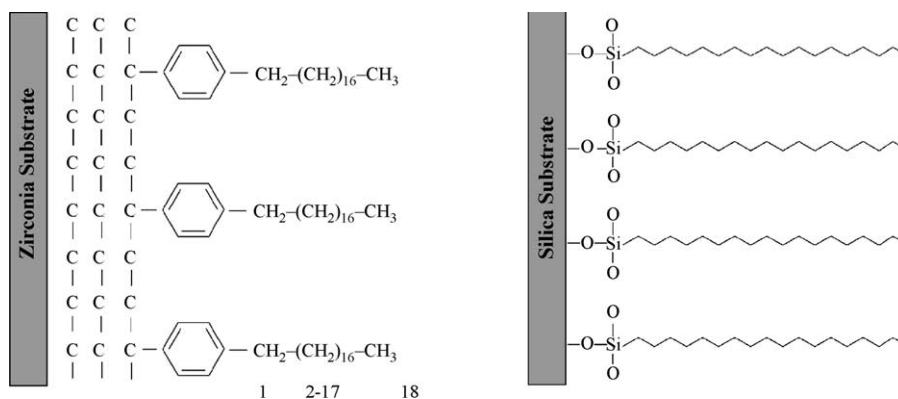


Fig. 1. Molecular structure of the zirconia and silica based systems.

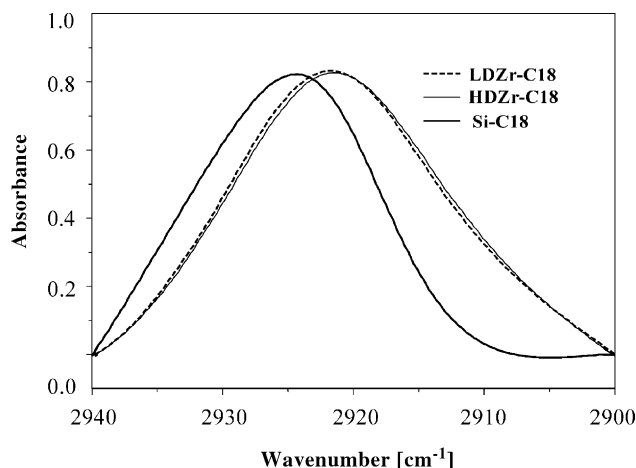


Fig. 2. Experimental CH₂ anti-symmetric stretching bands for LDZr-C18, HDZr-C18 and Si-C18 phases at 333 K.

For completely disordered structures the FT-IR frequency of the CH₂ anti-symmetric stretching band is close to that of a liquid alkane ($\nu_a = 2924 \text{ cm}^{-1}$). For well-ordered inter-phases the frequency is shifted to lower wave numbers and is close to that of crystalline alkanes ($\nu_a = 2915\text{--}2918 \text{ cm}^{-1}$). The same trend can be observed for the CH₂ symmetric stretching band as well. Thus, the frequency shift of the band maxima in the symmetric/anti-symmetric CH₂ stretching band regions ($2853\text{--}2846 \text{ cm}^{-1}$ and $2926\text{--}2912 \text{ cm}^{-1}$) provides qualitative information about the changes in the conformational order as a function of the sample temperature, surface coverage and solid supports. Fig. 2 portrays the FT-IR spectrum for the HDZr-C18, LDZr-C18 and Si-C18 in the anti-symmetric region between 2940 and 2900 cm^{-1} . The CH₂ anti-symmetric band maximum for both DiamondBond-C18 phases is almost the same whereas the band maximum varies by 4 cm^{-1} between silica based and zirconia based supports, i.e., DiamondBond-C18 phases. Upon increasing the sample temperature the corresponding absorption band maxima of the samples shifts towards higher wave numbers independent of the surface coverage. The position of the band maxima as well as the actual variation with temperature, however, depends on the respective samples. Fig. 3 depicts FT-IR spectra for the HDZr-C18 phases in the symmetric and anti-symmetric stretching band region between 3000 and 2800 cm^{-1} . The impact of temperature on the CH₂ symmetric and anti-symmetric stretching band maxima of the DiamondBond-C18 systems is found to be lower as compared to conventional C18-alkyl modified silica gels column materials.

It is important to note that the increase of FT-IR bandwidth with increasing temperature—a phenomenon described in the earlier studies [12,22,23] and in the present Si-C18 sample—is absent in the DiamondBond-C18 systems. In the case of Si-C18 (spectra not shown), the CH₂ bands are narrow at lower temperatures, reflecting a low alkyl chain flexibility and high conformational order [12]. At higher temperatures, an increase of CH₂ stretching bandwidth is observed which

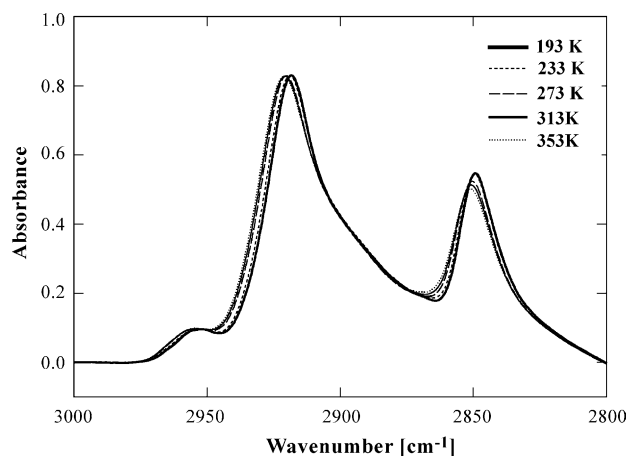


Fig. 3. Temperature dependence of the CH₂ symmetric and anti-symmetric stretching bands of HDZr-C18 phases.

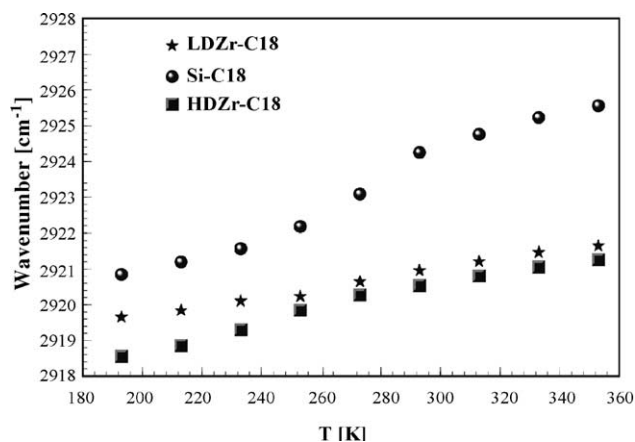


Fig. 4. Anti-symmetric CH₂ stretching band positions of LDZr-C18, HDZr-C18 and Si-C18 phases.

can be attributed to an enhanced alkyl chain flexibility owing to decrease of conformational order.

The derived results for the absorption frequencies of the CH₂ anti-symmetric and symmetric stretching band regions of the samples are summarized in Figs. 4 and 5.

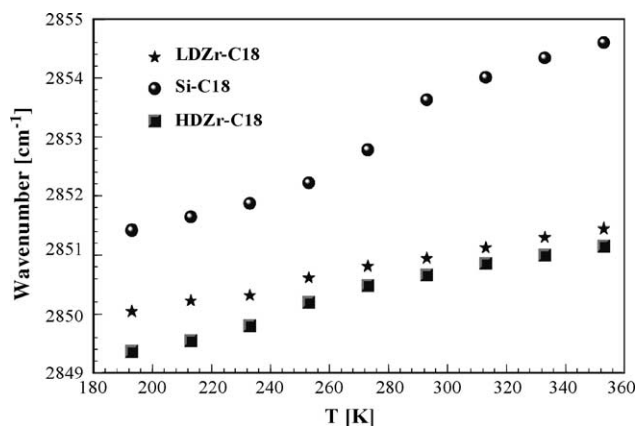


Fig. 5. Symmetric CH₂ stretching band positions of LDZr-C18, HDZr-C18 and Si-C18 phases.

Inspection of these figures reveals that the wave numbers of the symmetric and anti-symmetric stretching bands of the LDZr-C18, HDZr-C18 phases are lower as compared to the Si-C18 phases for the entire temperature range. These stretching band data imply that DiamondBond-C18 column materials exhibit a higher conformational order as compared to the C18-alkyl modified silica gels systems. Moreover, the impact of temperature on the silica-based systems is more pronounced as compared to the zirconia-based DiamondBond-C18 systems, which maintain their high conformational order over a wider temperature range. The existence of higher conformational order, in particular for a wider temperature range, is considered to be the molecular basis of the enhanced performance of the DiamondBond-C18 column materials during chromatographic separations [5,6].

In comparing the high and low bonding density DiamondBond-C18 systems, the HDZr-C18 has a slightly higher conformational order as compared to the LDZr-C18 systems. The surface coverage has a greater influence at lower temperatures as compared to higher temperatures. As expected, these results indicate that surface coverage has a direct influence on the conformational order of the alkyl chains. Even though the surface coverage is less in DiamondBond-C18 systems ($2.5 \mu\text{mol}/\text{m}^2$ for LDZr-C18, $4 \mu\text{mol}/\text{m}^2$ for HDZr-C18) as compared to Si-C18 ($4.2 \mu\text{mol}/\text{m}^2$), the influence of the solid supports dominates over the influence of surface coverage, as can be deduced from the present results. It should be emphasized that the alkyl modified silica gels and DiamondBond-C18 systems are chemically distinct from each other. As shown in Fig. 1, the zirconia particle surface is clad with a graphite-like layer linked with phenyl groups followed by tethered C18-alkyl chains, whereas the alkyl chains are directly connected to the surface silanol groups of the silica surface in the case of C18-alkyl modified silica gel.

Higher conformational order is observed for carbon clad zirconia-based systems when compared with silica based modified silica gels. One might be tempted to argue whether the ordering of alkyl chain originates from the zirconia supports or it stems from the carbon clad (graphite materials) that is coated on the surface of the zirconia supports. At present, a definitive answer on this issue cannot be given. The present findings, however, are consistent with previous data for C30 SAMs on different solid supports [12]. Here, it was clearly demonstrated that the substrate plays an important role on the conformational order of alkyl chains that are attached to the inorganic oxide surfaces. It was found that the highest conformational order exists on titania followed by zirconia and eventually by silica supports. Moreover, like in the present DiamondBond-C18 systems, a reduced temperature dependence of the alkyl chain conformations was observed for the C30 SAMs on zirconia and titania.

In the present systems an increase of conformational order is observed upon increase of surface coverage. This is consistent with the data from a comprehensive study on surface modified silica gels from our group [24]. Likewise, Fadeev et al. studied a series of zirconia-based samples that reacted with

octadecylsilane over different periods of time [25]. A gradual shift towards lower wave numbers was observed indicating a transition from completely disordered to ordered structures as the surface coverage of the monolayers increases.

One might wonder whether the CH_2 stretching band differences between the zirconia and silica based materials are due to the effect the carbon layer might have on the spectra and not a result of increased conformational order. However, earlier investigations on SAMs (also including different supports), biomembranes, alkanes and polymers [12,20,25,26] proved that the CH_2 stretching band positions are irrespective of the corresponding materials, and always occur in the same spectral range, as discussed earlier. Independent results from NMR [18,19] and Raman spectroscopy [13–16] as well as studies of other conformational sensitive IR bands clearly proved that the variation of the stretching frequencies is only due to changes in the conformational order. Remarkable changes in the CH_2 stretching absorption would be only expected if the respective support and the tethered alkyl chains strongly interact, for which there is no evidence in the present systems.

Variable temperature ^{13}C CP/MASNMR spectra of the LDZr-C18 material are depicted in Fig. 6. The ^{13}C NMR chemical shifts for $(\text{CH}_2)_n$ units of DiamondBond-C18 is observed at 30.2 ppm, which is attributed to gauche defects. The peak at 23.5 ppm characterizes the methylene unit attached to the phenyl group and the resonance at 13 ppm shows the presence of the terminal methyl group. The resonance at 129.5 ppm and the other resonances above 129.5 ppm occur due to the presence of the phenyl group and the graphite layers in the DiamondBond-C18 material (Fig. 1). The main signal for the $(\text{CH}_2)_n$ groups is almost unaffected by the actual sample temperature.

The ^{13}C CP/MASNMR spectra of the HDZr-C18 material is shown in Fig. 7, where the main resonance for the $(\text{CH}_2)_n$ is observed at 30.5 ppm, which is attributed to the disordered chain segments (liquid-like equilibrium of trans/gauche conformations). In comparison with the LDZr-C18 material, it is seen that the resonance frequency is slightly lowfield shifted, which suggests a reduced amount of disordered chain segments. Upon increase of temperature, the main resonance for the $(\text{CH}_2)_n$ is again practically unaffected. That is, the ^{13}C NMR data and the aforementioned FT-IR data for the DiamondBond-C18 samples provide consistent results with respect to the influence of temperature on the alkyl chain conformational order.

The variable temperature ^{13}C CP/MASNMR spectra of the Si-C18 (solution polymerised) are shown in Fig. 8. For the Si-C18 phases at room temperature, the NMR resonances for the main $(\text{CH}_2)_n$ resonance appear at 31.4 ppm, and at 13.2 ppm for the terminal CH_3 group. The value of 31.4 ppm for the main methylene resonance can be attributed to trans-gauche chains, which is in between the literature values for all-trans chains (~ 33 ppm) in crystalline alkanes and conformationally disordered gauche chains (~ 30 ppm) in isotropic melts [27]. For the present C18 chains, two

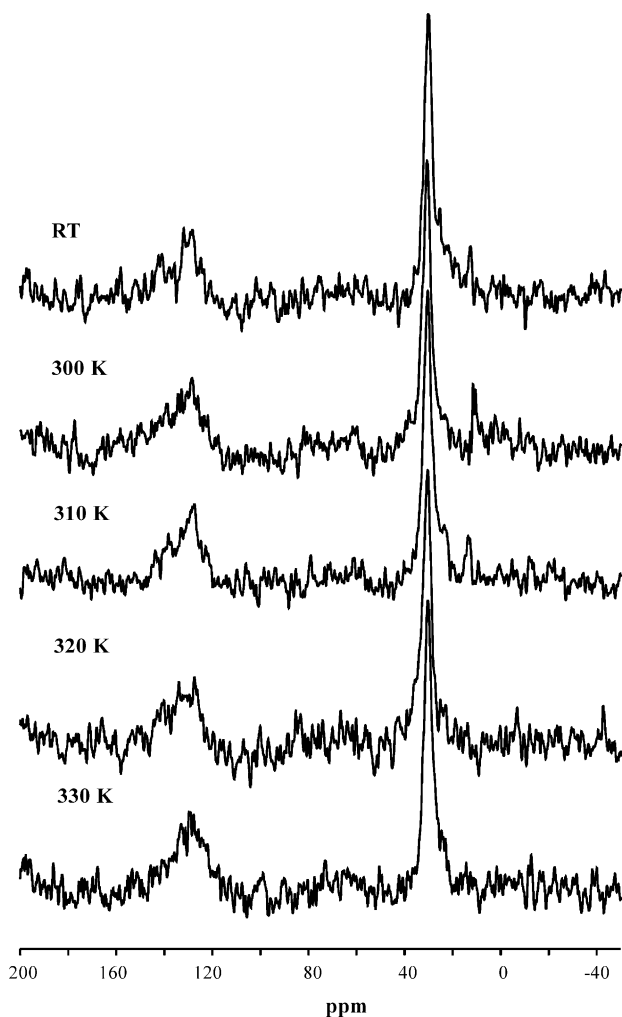


Fig. 6. Variable temperature ^{13}C CP/MASNMR spectra for the LDZr-C18 phases.

distinct methylene group signals, referring to these two types of alkyl chains of different conformational state, could not be observed simultaneously. Typically, such separated peaks only show up for longer alkyl chain lengths, such as C22, C30 or C34 [17,28,29]. Fig. 8 further demonstrates that the amount of gauche conformations increases with increasing temperatures, since the main resonance frequency shifts slightly upfield with a value of 31.0 ppm at 340 K. At higher temperatures, dual methyl resonance profiles are obtained at chemical shift values of 14.7 and 13 ppm.

On comparing the position of the main NMR resonances of the $(\text{CH}_2)_n$ groups in the DiamondBond-C18 phases and C18-alkyl modified silica gels, i.e., upfield shifts in the DiamondBond-C18 phases, one might be tempted to assign a “less ordered” organization to the methylene carbons $(\text{CH}_2)_n$ of DiamondBond-C18 phases and conclude that the DiamondBond-C18 phases have higher amounts of gauche concentrations. However, such upfield shifts for ^1H NMR resonances have been observed for adsorbates (chemisorbed) on other carbonaceous materials such as water on coles [30],

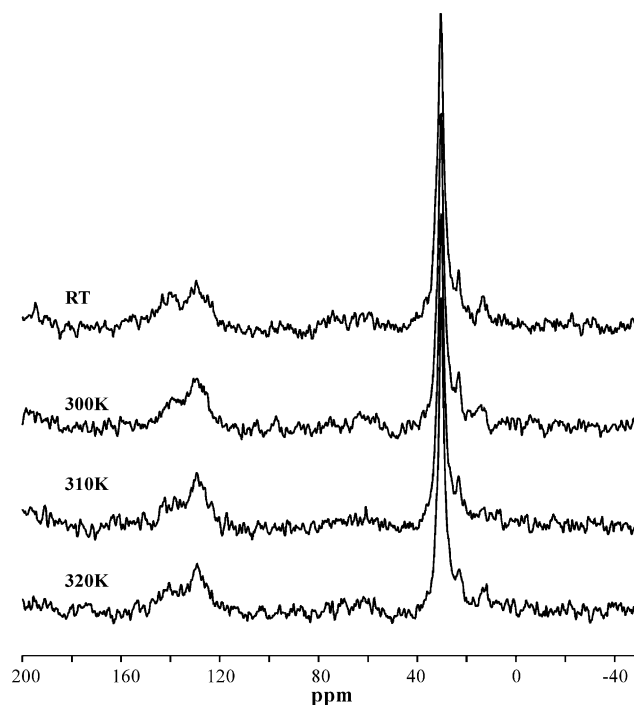


Fig. 7. Variable temperature ^{13}C CP/MASNMR spectra for the HDZr-C18 phases.

xenon on grafoil [31] and a variety of molecules adsorbed on the basal plane of graphite carbon black [32]. These findings were related to the existence of a highly anisotropic magnetic susceptibility of the ^{13}C CP/MASNMR powder pattern in graphite and related materials. As a result, the alkyl chains attached to the graphitic surface via phenyl group experience a strong diamagnetic field component due to the anisotropic magnetic susceptibility of the graphite layers [33]. Thus, the present overall upfield shift of the ^{13}C resonances of the DiamondBond-C18 phases does not reflect directly the conformational order. Rather it stems from the magnetic interaction with the graphite surface.

Therefore it is not possible to compare the ^{13}C CP/MASNMR spectra of the DiamondBond-C18 phases and the conventional C18-alkyl modified silica gels directly. Obviously, for the present systems the IR spectroscopic data, i.e., CH_2 stretching band positions, are more reliable. As mentioned earlier, the temperature dependencies of the ^{13}C resonances and CH_2 stretching band position for a distinct sample, however, are consistent.

Emphasis was also given to the terminal methyl group to understand the behaviour of alkyl chain structure especially on its surface. Dual methyl resonance peaks are observed only for silica based systems especially at higher temperatures i.e., above 330 K. Pursch et al. discussed the methyl group resonances in C30 SAMs in detail as an important characterization tool for these alkane-type SAMs [17]. Here, for C30 SAMs on ProntoSil (silica gel), dual methyl resonance profiles were observed at chemical shifts of 14.7 and ~ 13 ppm. A similar upfield shift has been noted for chain-end methyl

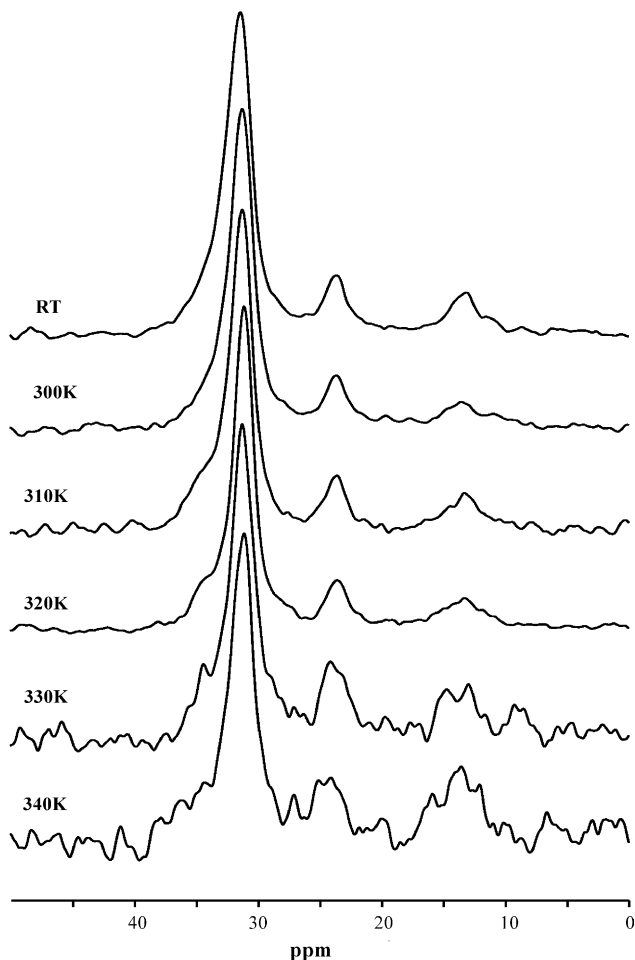


Fig. 8. Variable temperature ^{13}C CP/MAS NMR spectra for the Si-C18 phases.

groups in polyethylene when going from a crystalline to a noncrystalline environment [34]. The split up of the methyl resonance was attributed to the heterogeneity of the sample, i.e., methyl groups of different mobilities exist in these materials.

4. Conclusion

In the present study, two different C18-bonding density DiamondBond-C18 phases were examined by solid-state ^{13}C NMR and FT-IR spectroscopy. The temperature dependence of the ^{13}C NMR and FT-IR data was found to be consistent. However, contradictory results were obtained from the FT-IR and ^{13}C NMR data with respect to the influence of the solid support, which can be attributed to the existence of a highly anisotropic magnetic susceptibility of carbon cladding which is vapour deposited on the zirconia substrate. We conclude that the HDZr-C18 has a greater conformational order as compared to its corresponding low-density counterpart. The temperature dependence of the conformational order of the C18 chains on the carbon clad

zirconia phase is much less pronounced than in conventional column material prepared from silane modified silica gels. It is concluded that carbon clad zirconia based substrates exhibit a higher conformational order of alkyl chains and high thermal stability, which should be the molecular origin of the enhanced performance of the DiamondBond-C18 systems during chromatographic separations.

Acknowledgments

The Deutsche Forschungsgemeinschaft is gratefully acknowledged for the financial support. G.S. would like to thank the Graduiertenkolleg "Chemie in Interphasen" for a doctoral fellowship.

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