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Synthesis and spectrometric characterization of a true diol bonded phase

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Abstract

The syntheses of two types of diol bonded phases using a silanization/hydrosilation pathway are described. One product is similar to the phase produced by organosilanization but without the problem of potential side products and utilizes allyl glycidyl ether as the bonding olefin to the intermediate hydride. The second product is a "true" diol phase without any heteroatoms from the surface to the diol moiety and involves reacting 7-octene-1,2-diol with hydride silica. Both products can be obtained in good yield and the bonded phases can be characterized spectrometrically by diffuse reflectance IR Fourier transform and cross-polarization magic angle spinning NMR spectrometry. The only complication to this reaction scheme is bonding of the olefin diol to the silica surface via one of the alcohol groups (esterification). It appears that this is a problem when the original silica contains a significant number of unassociated silanol groups.

1. Introduction

The use of epoxy and/or diol phases in HPLC has been established for many years [1,2]. The normal synthetic route involves bonding of 3-glycidyloxypropyltrimethoxysilane to silica followed by hydrolysis of the epoxide ring to form the diol [2]. The epoxide is a useful intermediate for the production of certain ion-exchange [3] or affinity phases [4–7]. In earlier studies it was suggested that bonding of the silane to silica under slightly acidic conditions (pH 5–6) was necessary to preserve the oxirane ring [3,4,8]. However the presence of the reactive epoxide species leads to complications in the bonding reaction that can often lead to a variety of products instead of the desired epoxy or diol

materials. A recent study has shown that temperature, pH and solvent all have a considerable effect on the presence and nature of species other than the intermediate epoxide or the diol bonded phases [9]. Among the species identified on the silica surface were various glycol ethers, polyaddition products, and cyclic oligosilanes. Therefore, it is not surprising that diol phases from different sources, and perhaps even different batches, display varying degrees of hydrophilic and hydrophobic properties. In order to solve the problem of variability in the diol product phase, another approach to synthesizing this material is needed.

The reactive glycidyloxypropyl and trimethoxy species on the bonding moiety complicate the process which leads to the formation of more than one product. A possible solution to this problem is to replace the organosilanization
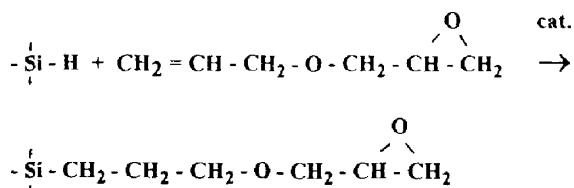
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process by a silanization/hydrosilation reaction scheme [10]. This approach eliminates the organosilanization reagent and immediately removes the possibility of reactions involving the trimethoxy species. The key to this synthetic scheme is the formation of a hydride intermediate on the silica surface. This can be accomplished by the reaction of silica in the presence of the hydrolysis product of triethoxysilane (TES) under carefully controlled conditions. The reaction can be described as follows:

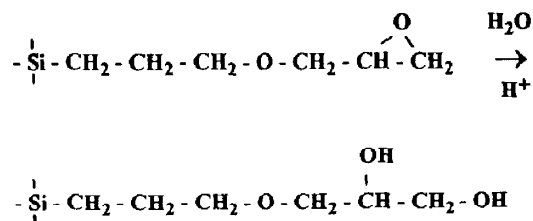$$- Si - OH \ + \ (HO)_3 - Si - H \ \rightarrow \ - Si - O - Si - H$$
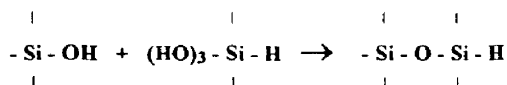
With the correct TES:silica ratio and the appropriate concentration of acid catalyst, a monolayer of hydride can be formed on the surface. The net effect is to essentially replace all of the silanols with hydrides on the surface. While 100% efficiency is not possible due to incomplete condensation of TES on the surface, the small size of hydride in comparison to other organic moieties makes this process much more efficient than typical organosilanization reactions [10]. Indeed, not all silanols can be removed from silica because some are "buried" in micropores that would be inaccessible to the silanization reagent (hydrolysis product of TES). However, in theory very few accessible silanols should be present on the silica surface when compared to bonded phases produced by organosilanization.

Once the hydride intermediate has been formed, then there are two options for forming a diol bonded material. The first is a synthetic path similar to the one used for preparation of epoxy and diol phases by the conventional method. It involves bonding allyl glycidyl ether (AGE) to the hydride intermediate as follows:
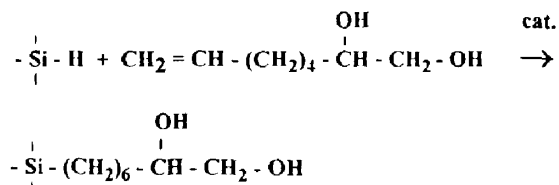
$$- Si - H \ + \ CH_2 = CH - CH_2 - O - CH_2 - CH - CH_2 \ \xrightarrow{\ cat.\ } $$

$$- Si - CH_2 - CH_2 - CH_2 - O - CH_2 - CH - CH_2$$

After bonding of the oxirane compound, then formation of the diol can be accomplished by opening of the epoxide ring in acid solution:

$$- Si - CH_2 - CH_2 - CH_2 - O - CH_2 - CH - CH_2 \ \xrightarrow[H^+]{H_2O} $$

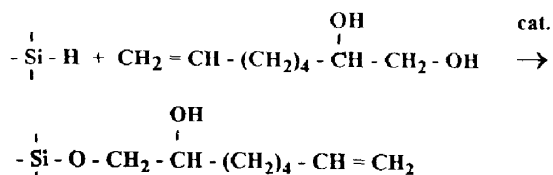$$- Si - CH_2 - CH_2 - CH_2 - O - CH_2 - \overset{OH}{CH} - CH_2 - OH$$

While this general procedure is similar to that of the organosilanization reaction, it eliminates those side reactions which involve the trimethoxy reactive groups on the organosilane. However, care must still be exercised when bonding the olefin since too high of a concentration of this species can result in polymerization rather than monomeric bonding. Even if the bonding scheme works perfectly, the final product is not a true diol since the ether linkage is still present leading to a slightly higher hydrophilicity. However, this reaction scheme still preserves the option of utilizing the epoxide moiety as a binding site in such applications as affinity chromatography.

The possibility of forming a true diol bonded phase can be realized by reacting the hydride intermediate with 7-octene-1,2-diol (7-OD).

$$- Si - H \ + \ CH_2 = CH - (CH_2)_4 - \overset{OH}{CH} - CH_2 - OH \ \xrightarrow{\ cat.\ }$$

$$- Si - (CH_2)_6 - \overset{OH}{CH} - CH_2 - OH$$

In this procedure the olefin is presumably the most reactive site and hydrosilation is the preferred pathway leading to the formation of the diol bonded phase. The absence of other functional groups or heteroatoms on the above product results in a "true" diol bonded phase. Some caution must be exercised in this reaction scheme since bonding via the terminal hydroxy group is possible leading to a silicon–oxygen–carbon linkage at the surface [11] and an olefin at the opposite end of the organic moiety.

$$\overset{\displaystyle\quad\quad\quad\quad\overset{OH}{|}\quad\quad\quad\quad cat.}{-\underset{|}{\overset{|}{Si}}-H\ +\ CH_2=CH-(CH_2)_4-\overset{|}{CH}-CH_2-OH\quad\longrightarrow}$$

$$\overset{\displaystyle\quad\quad\quad\quad\quad\overset{OH}{|}}{-\underset{|}{\overset{|}{Si}}-O-CH_2-\overset{|}{CH}-(CH_2)_4-CH=CH_2}$$

Since such competitive reactions have not been studied before on silica, careful spectrometric characterization of the hydrosilation product must be undertaken to determine if esterification contributes significantly to the population of bonded organic species.

2. Experimental

Solid-state NMR spectra, cross-polarization (CP) with magic angle spinning (MAS) were obtained on a Bruker MSL 300 spectrometer. Samples of 200–300 mg in a double bearing ZrO_2 rotor were measured at a spinning rate of 5 kHz. For ^{13}C spectra the contact time was 5 ms with a repetition rate of 5 s. The chemical shifts were referenced to tetramethylsilane by using the carbonyl signal of glycine as a standard. For ^{29}Si, CP-MAS-NMR spectra were recorded using a contact time of 5 ms and a pulse repetition rate of 5 s with poly(hydrido)siloxane as the standard.

Diffuse reflectance IR Fourier transform (DRIFT) spectra were obtained with a Perkin-Elmer Model 1800 Fourier transform (FT) IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. Spectra were taken in the 4000–450 cm^{-1} region with a nominal resolution of 2 cm^{-1}. Two hundred sample

scans were acquired against pure KBr as a reference. Spectra were normalized to 100% transmittance.

Carbon analysis was carried out by a conventional combustion method with a Perkin-Elmer Model 240C elemental analyzer equipped with a Model 56 recorder. Samples of 5–15 mg were analyzed.

2.1. Materials

The silica gels used are listed in Table 1. The samples were dried in a vacuum oven at 110°C for 48 h before the silanization. AGE and 7-OD (both Aldrich) were used to prepare the bonded silicas. A 10 mM hexachloroplatinic acid (3.75% as Pt, Aldrich) solution in 2-propanol was used as the catalyst for the hydrosilation reaction. p-Dioxane (J.T. Baker) was dried by contact with calcium hydride (Sigma) for several days and then distilled before use. TES (Huls America) was used as received. Distilled water was purified in the laboratory using a Millipore Model Milli-Q deionization system.

The concentration of surface-bonded groups was obtained from carbon percentages determined from elemental analysis according to the equation of Berendsen and De Galan [12]. The specific surface area used in the calculation was the value given by the supplier. See Table 2.

Hydride silica intermediates were prepared by a previously reported silanization method [10]. The hydride-modified supports were formed by reacting TES (45 ml of 0.5 M TES/dioxane solution) with the silica substrates (5.00 g of each silica) in the presence of water, an acid catalyst

Table 1
Physical characteristics of bare silica gels

No.	Type	Porosity			Supplier
		d_p	S_{BET}	D	
1	Vydac 101 TP, lot 900 201	6.58	106.5	380	Separations Group (Hesperia, CA, USA)
2	Davisil, grade 633	32–74	480.0	60	Aldrich (Milwaukee, WI, USA)

d_p = Particle diameter (μm); S_{BET} = specific surface area (m^2/g); D = pore diameter (Å). All data from supplier.

Table 2
Carbon content and surface coverages (α_R) of diol silica samples

No.	Sample	Corrected (% C)[a]	α_R (μmol/m^2)
1	Vydac-diol (AGE)[b]	4.16	5.87
2	Vydac-diol (AGE)	2.18	2.96
3	Davisil-diol (AGE)	7.24	2.41
4	Vydac-diol (7-OD), grey	3.35	3.45
5	Davisil-diol (7OD), grey	10.10	2.58
6	Vydac-diol (7OD), white	3.54	3.65
7	Davisil-diol (7OD), white	9.77	2.48
8	Vydac-diol (7OD), white, large batch	4.08	4.25

[a] % C after subtracting the amount before hydrosilation reaction.
[b] Possible polymerization of AGE.

(7 ml of 2.3 M HCl solution) and dioxane (100 ml). Under those experimental conditions an SiH monolayer was covalently bonded to the silica surface. The final product was washed consecutively with 50-ml portions of water–tetrahydrofuran (THF) (20:80), THF and diethyl ether (twice with each solvent), dried at room temperature and then in a vacuum oven at 110°C for at least 6 h.

The chemically bonded phases were synthesized by a modification of previous methods [13,14]. The solution of olefin (2.65 ml) in toluene (40.82 ml) and catalyst (1.53 ml of 10 mM H$_2$PtCl$_6$) was heated to about 60–70°C while being magnetically stirred for 1 h, then the sample of hydride modified silica (2.60 g) was slowly added. The reaction was allowed to proceed for 96 h at 90 ± 1°C. After this time period the solvent was removed and the solid washed with 30-ml portions of toluene (three times) followed by similar washings with dichloromethane and diethyl ether. The product was dried at room temperature first for 1 h and then under vacuum at 110°C overnight. The chemical surface modification with AGE was carried out in standard glassware as described above but under nitrogen. The hydrolysis of AGE to form the diol consisted of placing the epoxy material in a stirred 0.05 M HCl solution at 65 ± 1°C for 4 h.

3. Results and discussion

In order to properly interpret the spectral results of the product phases, it was necessary to first characterize the hydride intermediate. A surprising result was obtained in routine carbon analysis when both the bare silica and the hydride were used for background measurements in the determination of the ligand concentration on the product phases. The bare Davisil did not have a measurable amount of carbon while the hydride intermediate had 0.4% C after silanization with TES. The bare Vydac silica and the hydride contained 0.3 and 1.0% carbon respectively. The presence of the carbon containing material was confirmed by DRIFT spectra in all cases when peaks in the 3000–2800 cm^{-1} range were observed. In the case of Vydac material, the ^{13}C CP-MAS-NMR spectrum (Fig. 1A) of the bare silica displays a prominent peak at about 50 ppm (most likely a methoxy group) while the spectrum of the hydride material (Fig. 1B) shows peaks at 17 and 60 ppm (also detectable in the bare silica spectrum). These latter chemical shifts correspond to the methyl and methylene resonances of the ethoxy moiety. The presence of the ethoxy species on the surface can be accounted for by either incomplete hydrolysis of TES or by subsequent bonding of the ethanol released during TES hydrolysis to the silica surface. What was even more surprising was that these peaks persisted even after extensive washing under aqueous conditions since the ethoxy moiety is bonded to the silica surface via a labile Si–O–C linkage. Even though some carbon is detected by elemental analysis and DRIFT for the Davisil hydride, no peaks were observed in the ^{13}C CP-MAS-NMR spectrum which indicates that residual ethoxy species are not a significant factor on this material.

Each of the two proposed reaction schemes for producing the diol on hydride-modified silica were tested and studied spectrometrically. The following sections summarize the DRIFT and CP-MAS-NMR results for the two types of diol.

3.1. Diol via allyl glycidyl ether
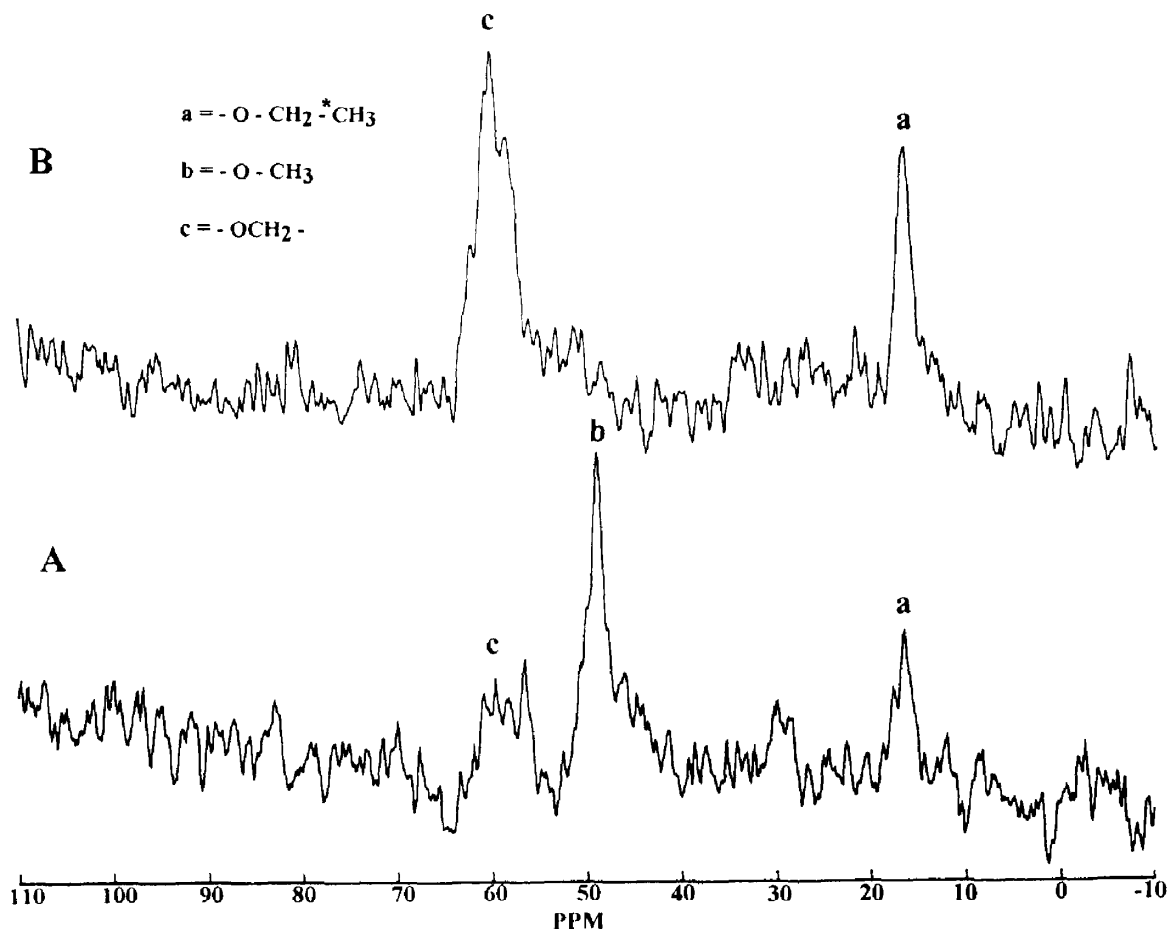
The differences between the final material

c

a = - O - CH$_2$ -*CH$_3$

B

b = - O - CH$_3$

c = - OCH$_2$ -

a

b

A

c

a

```
110   100    90    80    70    60    50    40    30    20    10     0    -10
                                    PPM
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Fig. 1. ^{13}C CP-MAS-NMR spectra of bare (A) Vydac silica and the same material after reaction with the hydrolysis product of triethoxysilane (B).

produced by the silanization/hydrosilation and organosilanization processes revolve mainly around the number of possible bonded moieties. As enumerated above, the latter process can lead to several different species in varying proportions on the silica surface depending on the reaction conditions [9]. However, the hydride-based material generally leads to only a single bonded material if the concentration of AGE is kept low. Then polymerization of this molecule will be limited with only the epoxy bonded phase on the surface.

Fig. 2 shows the DRIFT spectrum of the hydride intermediate on Davisil silica (spectrum A). The characteristic Si–H stretching frequency is readily apparent at 2250 cm^{-1}. Upon reaction with AGE, the Si–H peak diminishes in intensity and strong C–H stretching bands appear in the 3000–2800 cm^{-1} range as shown in Fig. 2 (spectrum B). These results indicate successful formation of at least the epoxide bonded phase. Evaluation of the extent of the hydrolysis process cannot be made from these spectra. A similar analysis can be made of the DRIFT spectra for the same reactions on Vydac silica. It is also not possible to ascertain conclusively from the DRIFT spectra whether any side reactions or polymerization have taken place during the bonding process.

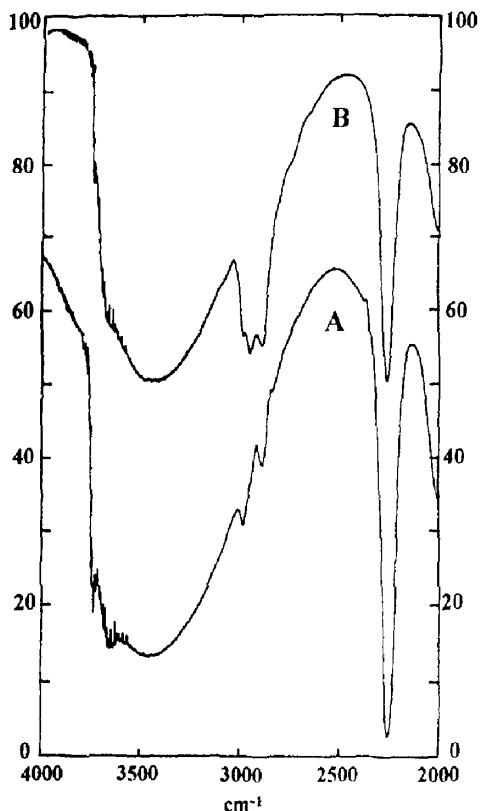The hydrosilation process results in a direct

Fig. 2. Partial DRIFT spectra of hydride intermediate on Davisil (A) and the product obtained from the reaction with AGE (B).

silicon–carbon bond at the surface. This can be easily detected in the ^{29}Si CP-MAS-NMR spectrum. Fig. 3 shows the ^{29}Si NMR spectra of the AGE product on both Davisil (A) and Vydac (B) silicas. In both spectra the peak for the silicon atom directly bonded to carbon can be seen at −65 ppm. The intensity of this peak is low because there are relatively few protons close-by to provide the cross-polarization necessary for increased sensitivity. In addition to the appearance of the new peak at −65 ppm, a decrease in the Si–H peak intensity at −85 ppm is also observed. This is expected since success of the hydrosilation reaction converts hydride sites into bonded organic moieties.

Fig. 4 shows the ^{13}C CP-MAS-NMR spectrum of the AGE moiety bonded on Vydac silica and subsequently hydrolyzed by HCl. This spectrum can be used to confirm both the success of the

bonding reaction as well as the hydrolysis from the epoxide to the diol. The peaks for the ethoxy group identified on the hydride can be seen at 16 and 60 ppm. The peak at 7 ppm represents the carbon directly bonded to the silica surface. The peak at 22 ppm is due to the methylene group next to the surface bonded carbon. The peaks at 71 ppm and 65 ppm (shoulder) are due to the remainder of the carbon atoms in the molecule. Each of these carbons is bonded to an oxygen atom and accounts for the downfield chemical shift. If the hydrolysis reaction is not complete a peak at 45 ppm indicates the presence of the epoxide bonded material [8,15,16]. Absence of this peak indicates success of the acid hydrolysis and the presence of the resulting diol.

3.2. Diol via 7-octene-1,2-diol

The results above indicate the ease of bonding the AGE moiety to either a wide-pore (Vydac) or a narrow-pore (Davisil) silica as well as the success of hydrolyzing the epoxide ring to the diol product. However, the final bonded moiety is not a true diol since it is composed of two three-carbon chains connected via an ether linkage. Because of the versatility of the hydrosilation reaction in the presence of the hydride surface, it is possible to make a true diol phase, i.e. with no heteroatoms between the silica and the 1,2-diol moiety, using a terminal olefin with two OH groups on the last two carbons at the opposite end of the molecule. To test this possibility, 7-OD was chosen as the olefin to be bonded. This molecule possess a hydrocarbon chain which is long enough so that the diol functionality is significantly removed from the surface with a hydrophobic buffer in-between.

Fig. 5 shows the DRIFT spectra of products from the reaction of 7-OD on both Davisil hydride (A) and Vydac hydride (B). In both cases, a comparison with the starting hydride shows a decrease in intensity of the Si–H band at 2255 cm^{-1} and a concomitant appearance of C–H stretching bands between 2800–3000 cm^{-1}. These results conclusively prove that bonding of a diol-containing olefin can be readily accomplished on a hydride-modified silica surface.
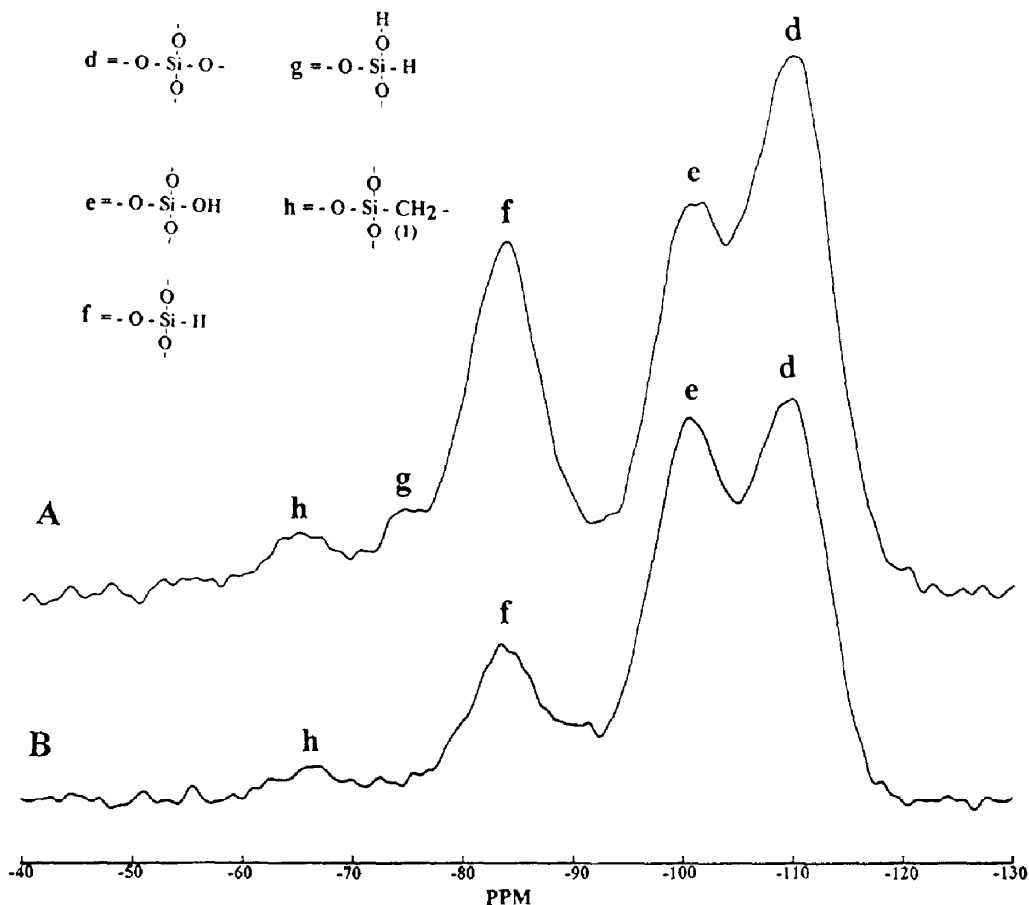
Fig. 3. ^{29}Si CP-MAS-NMR spectra of the products from the reaction of the hydride intermediate and AGE on Davisil (A) and Vydac (B) silicas.

However, closer examination of the C–H stretching region in the DRIFT spectra (Fig. 6) of the Davisil diol shows an additional band above 3000 cm^{-1}. Its location at 3080 cm^{-1} corresponds to the expected position of an allylic functional group. While its intensity is low, it does indicate that at least a small amount of the olefin is bonded via one of the OH groups. Since most of the silanols on the bare silica have been replaced by hydrides, it is not surprising that only a small amount of the olefin is bonded via a Si–O–C linkage. Nevertheless, this result proves that there is a competition between the hydrosilation and the silanol/alcohol condensation reactions. However, the same effect is not observed on the Vydac silica. This may be due to the fact the bare Vydac silica contains relatively few isolated silanols or impurities on the surface in comparison to Davisil silica. Therefore, the silanols which remain after TES silanization on Vydac are probably still the less-reactive associated Si–OH's.

Further confirmation of the bonding process involving hydrosilation with 7-OD can be acquired from CP-MAS-NMR spectra. Fig. 7 shows the ^{29}Si CP-MAS-NMR spectra of both the Vydac (A) and Davisil (B) products. In each case there is a decrease in the intensity of the peak at −85 ppm (O$_3$–Si–H) and the appearance of a new peak at −65 ppm (O$_3$–Si–C–). A similar conclusion about the intensity of the peak at −65 ppm to that for the AGE product can be made for 7-OD. That is its intensity is low because there are relatively few protons nearby.
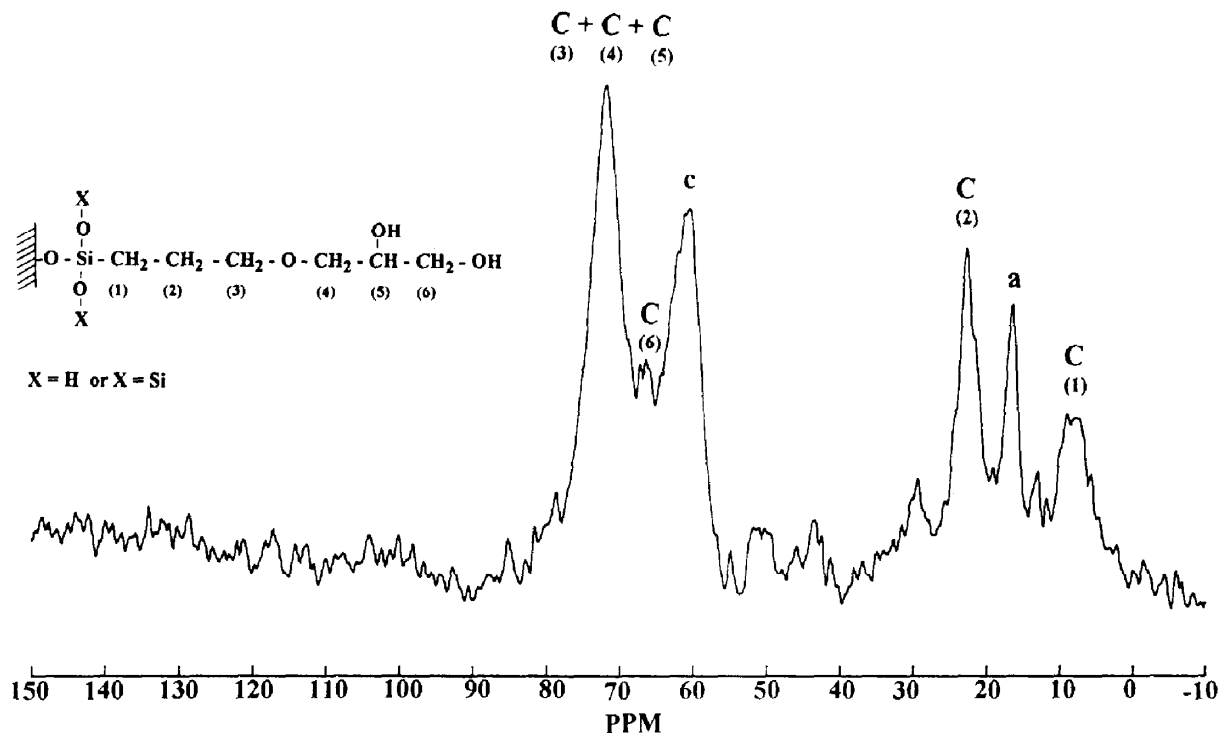
Fig. 4. ^{13}C CP-MAS-NMR spectrum of the product from the reaction of the hydride intermediate on Vydac silica and AGE after hydrolysis.

However, its appearance in the spectrum proves the success of the hydrosilation reaction.

Fig. 8 shows the ^{13}C CP-MAS-NMR spectrum for the same two products. A peak for the Si–C linkage can be seen at 12 ppm in the Davisil spectrum (A). The remainder of the methylene groups appear between 22–32 ppm. Two peaks for the–CH_2–OH and–CH(OH) groups appear at 67 and 72 ppm, respectively. In fact, with the shoulder on the 32 ppm peak, resonances for each of the eight carbons in the molecule can be identified. The Davisil spectrum contains two extra peaks at 124 and 132 ppm. These peaks are in the olefinic region of the spectrum and give further support to the conclusion that some of the 7-OD bonds via one of the alcohol groups to form an esterification product. In some cases two additional peaks can be observed at 113 and 136 ppm suggesting that perhaps bonding can occur at either alcohol group. Spectrum B in Fig. 8 is the spectrum which results from bonding 7-OD to Vydac hydride. The same peaks enumerated
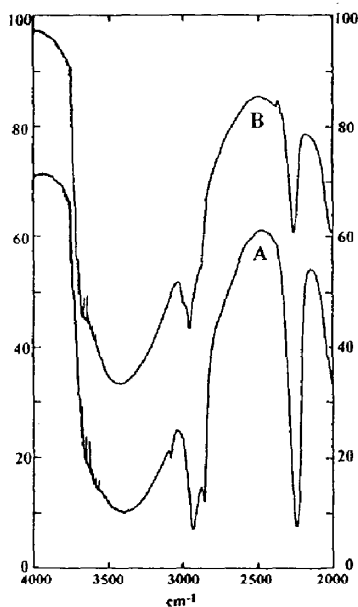

Fig. 5. Partial DRIFT spectra of the products from the reaction of the hydride intermediate and 7-OD on Davisil (A) and Vydac (B) silicas.
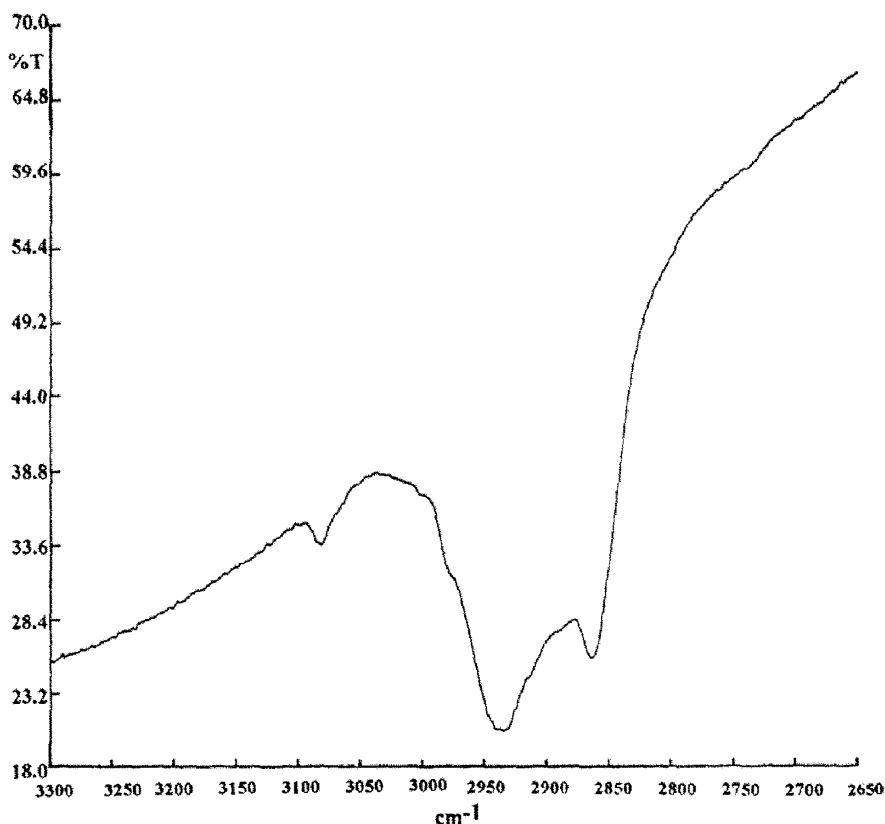
Fig. 6. Partial DRIFT spectrum of C–H stretching region of the product from the reaction of the hydride intermediate on Davisil and 7-OD. T = Transmittance.

above which document the success of the hydrosilation reaction can be identified in this spectrum as well. In addition, the two peaks for the ethoxy moiety can be seen at 16 and 60 ppm. However, no peaks are seen in the olefinic portion of the spectrum. This confirms the results obtained by DRIFT for the two materials which indicate some bonding through one of the alcohols for Davisil but not for Vydac.

3.3. Catalyst reduction

A known complication of the hydrosilation reaction for the bonding of olefins to hydride silica is the possible reduction of the catalyst to the elemental state and resulting deposition on the surface [13]. At high concentrations of catalyst (100 mM), the surface of Vydac and Davisil silica became gray for both the AGE and the 7-OD reactions. Fig. 9 shows the ^{29}Si CP-MAS-NMR spectrum of the 7-OD reaction product on Vydac hydride in the presence of high catalyst concentration. A large decrease in the Si–H peak at −85 ppm can be seen. The material has a very noticeable grey color which lends further support to the assumption that some reduction of Pt(IV) to Pt(0) has taken place. Absolute confirmation of this result was determined from the electron spectrometry for chemical analysis (ESCA) spectrum of this and other gray products which were obtained from AGE and 7-OD reactions at high catalyst concentration. Quantitative measurements of Pt on the surface ranged from 0.01 to 0.12 atom%. Therefore, all subsequent syntheses were done with 10 mM of catalyst and in each case the products obtained were white with no detectable Pt on the surface by ESCA.
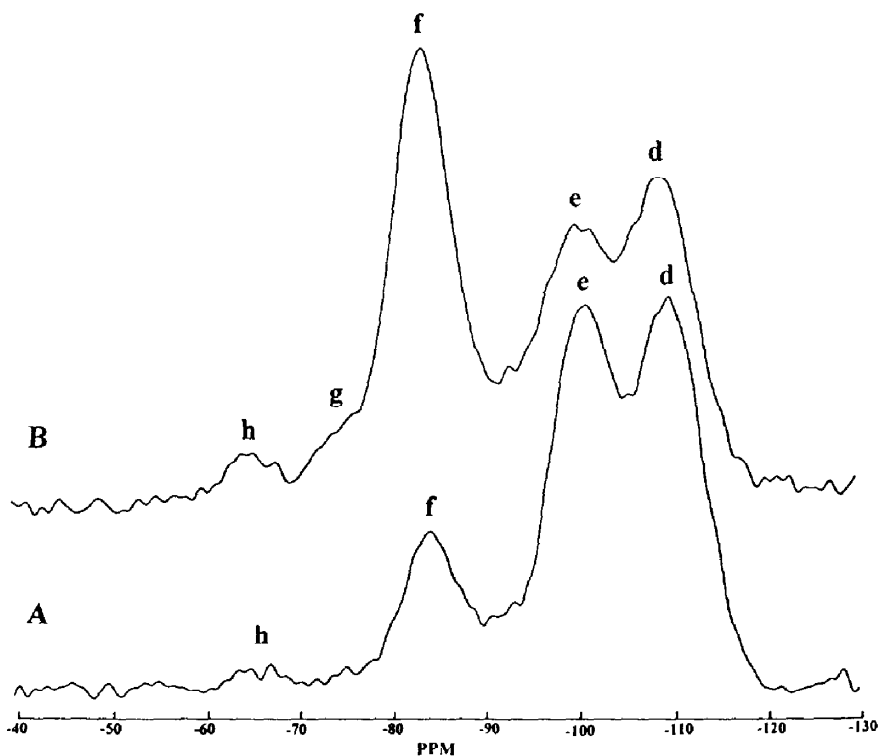
Fig. 7. ^{29}Si CP-MAS-NMR spectra of the products from the reaction of the hydride intermediate and 7-OD on Vydac (A) and Davisil (B) silicas.
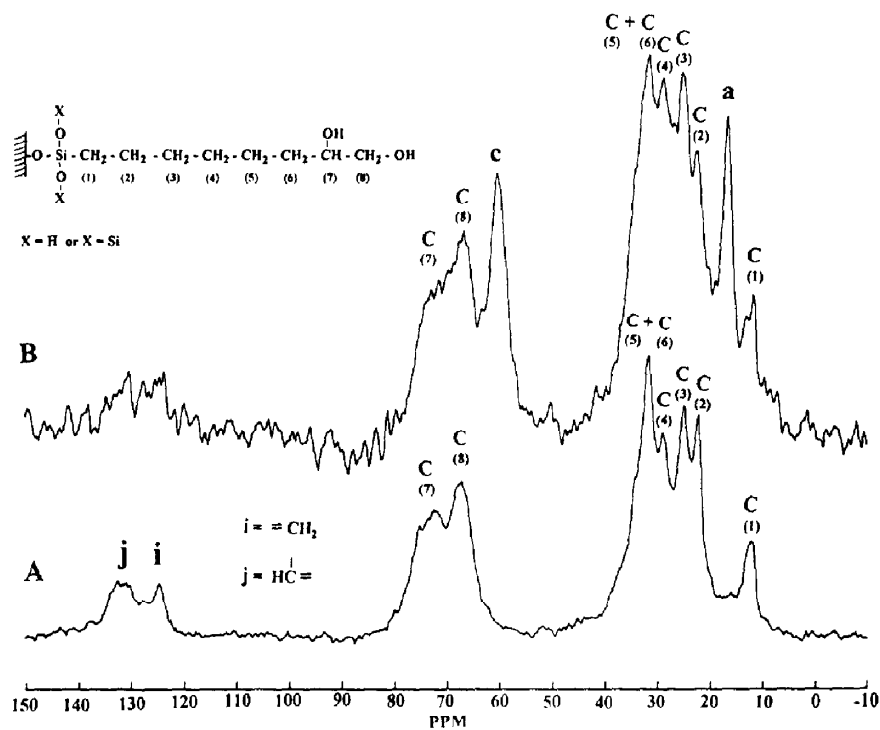

Fig. 8. ^{13}C CP-MAS-NMR spectra of the products from the reaction of the hydride intermediate and 7-OD on Davisil (A) and Vydac (B) silicas.
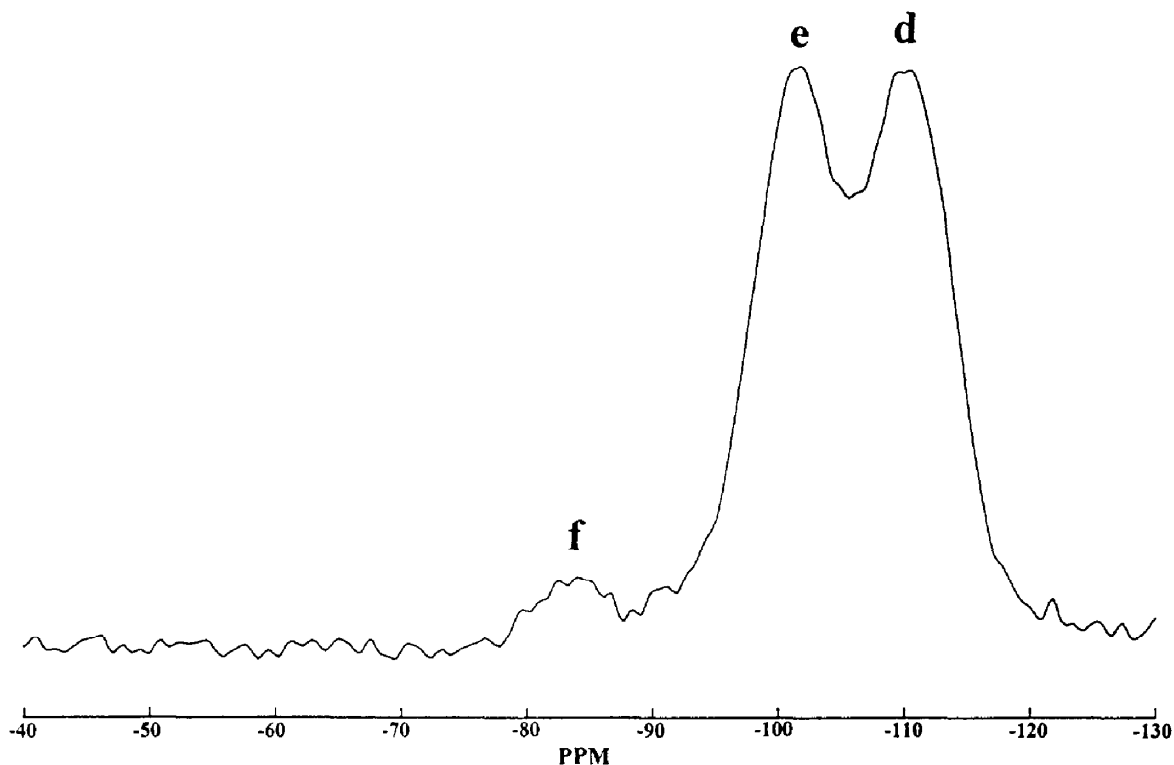
Fig. 9. ^{29}Si CP-MAS-NMR spectrum of the product from the reaction of the hydride intermediate and 7-OD on Vydac silica in the presence of high catalyst concentration.

In conclusion, the above synthetic pathways provide two options for synthesizing potentially uniform and reproducible bonded diol phases for chromatography. Both proceed through the hydride intermediate and via hydrosilation under transition metal catalysis to the final product. Each method is successful if the catalyst concentration is not too high to prevent reduction and deposition of the reduced metal on the surface. The two products are slightly different in that the AGE material has an ether linkage between two three-carbon chains while the 7-OD phase contains only methylene groups until the final two carbons which have the alcohol groups. In the latter reaction, the degree of hydrophobicity vs. hydrophilicity could be controlled by varying the length of the hydrocarbon chain in the original olefin. The only complication of the 7-OD reaction appears to be the potential competition from bonding through the alcohol groups (esterification). However, it appears that if the original silica contains very few unassociated (free) silanols then this reaction is minimized, i.e. undetectable by either DRIFT or ^{13}C CP-MAS-NMR analysis.

Acknowledgements

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