Published in final edited form as:

Electrophoresis. 2014 September ; 35(18): 2579–2586. doi:10.1002/elps.201400216.

Novel 3-hydroxypropyl bonded phase by direct hydrosilylation of allyl alcohol on amorphous hydride silica

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Abstract

A novel 3-hydroxypropyl (propanol) bonded silica phase has been prepared by hydrosilylation of allyl alcohol on a hydride silica intermediate, in the presence of platinum (0)-divinyltetramethyldisiloxane (Karstedt's catalyst). The regio-selectivity of this synthetic approach had been correctly predicted by previous reports involving octakis(dimethylsiloxy)octasilsesquioxane ($Q_8M_8^H$) and hydrogen silsesquioxane (T_8H_8), as molecular analogs of hydride amorphous silica. Thus, C-silylation predominated ($\sim 94\%$) over O-silylation, and high surface coverages of propanol groups ($5 \pm 1 \mu\text{mol}/\text{m}^2$) were typically obtained in this work. The propanol-bonded phase was characterized by spectroscopic (IR and solid state NMR on silica microparticles), contact angle (on fused-silica wafers) and CE (on fused-silica tubes) techniques. CE studies of the migration behavior of pyridine, caffeine, tris(2,2'-bipyridine)Ru(II) chloride and lysozyme on propanol-modified capillaries were carried out. The adsorption properties of these select silanol-sensitive solutes were compared to those on the unmodified and hydride-modified tubes. It was found that hydrolysis of the SiH species underlying the immobilized propanol moieties leads mainly to strong ion-exchange based interactions with the basic solutes at pH 4, particularly with lysozyme. Interestingly, and in agreement with water contact angle and electroosmotic mobility figures, the silanol-probe interactions on the buffer-exposed (hydrolyzed) hydride surface are quite different from those of the original unmodified tube.

Keywords

Bonded phases; Capillary electrophoresis; Hydrosilylation; Silica hydride; Silsesquioxanes

1 Introduction

Hydridosilica-based bonded phases bearing direct silicon-carbon linkages have been prepared in the past by the catalytic addition of silicon hydride to a terminal olefin, a reaction known as hydrosilylation. In addition to the high hydrolytic stability of the silicon-carbon linkage formed, the great versatility of the process has resulted in the synthesis of a

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This article is dedicated to the memory of Professor Rodrigo Paredes.

Conflict of interest statement

The authors have declared no conflict of interest.

variety of bonded phases useful for LC as well as CE. Organic groups range from simple hydrocarbons such as octyl, octadecyl or adamantyl to make bonded silicas useful for reversed-phase LC [1–4], to more reactive ones such as methacrylate [5] and glycidyl ether [6] to obtain coatings applicable to CE after further modification. For instance, once anchored onto the surface the methacryl group can copolymerize with acrylamide-related monomers to generate surfaces coated with a hydrophilic polymer useful for the CE separation of biomolecules such as proteins and their fragments [5]. Likewise, the epoxy group can be covalently attached to protein ligands with specific biological activity useful in affinity chromatography or electrophoresis. Alternatively, the epoxy group can be hydrolyzed under mild conditions to generate diol groups useful as a monomeric hydrophilic coating for a variety of separations [6]. Other organic functional groups attached to the silica surface via hydrosilylation include but are not limited to menthyl ether [7], cholesteryl [8], (methacryloyloxy)ethyl succinate [9], fullerene C60 [10], etc.

Over the last two decades, the chemical processes that take place at the silica surface have been studied using silsesquioxanes as molecular analogs to amorphous silica due to their structural similarities. Silsesquioxanes are molecular compounds that possess a cage-like silicon-oxygen framework with general formula $(\text{RSiO}_{3/2})_n$ and well-established chemistry [11,12]. The R-group may be a diversity of functionalities such as hydrogen, alkyl, aryl or silyl. For instance, cubic silsesquioxanes ($n = 8$), have been extensively used as molecular models for heterogeneous silica-supported catalysts [12]. Incompletely condensed silsesquioxanes containing various silanols have also been successfully applied as homogeneous models for silica surface silanol sites [11]. Not only silsesquioxanes serve as molecular models to explain many processes occurring on amorphous silicas, but they should also predict new ones. Remarkably, the reaction of octakis(dimethylsiloxy)-octasilsesquioxane, $\text{Q}_8\text{M}_8^{\text{H}}$, ($\text{R} = \text{HSiMe}_2\text{O}$) with allyl alcohol [13] has led to exclusive C-silylation to give octakis(3-hydroxypropyl-dimethylsiloxy)octasil sesquioxane, with virtually no competition of O-silylation. Similar regio-selective hydrosilylation at the double bond of allyl bromide was demonstrated for $\text{Q}_8\text{M}_8^{\text{H}}$ as well as for its analogous T_8H_8 ($\text{R} = \text{H}$) [14]. Although the products of these reactions were devised as macromonomers to produce organic/inorganic nanocomposites [13,14], their syntheses clearly forecasted a regio-selective hydrosilylation at the double bond of allyl groups on a hydride silica support. Thus, in the present work, we hypothesize that the C-silylation predicted from hydride-functionalized molecular sesquioxanes is also exhibited by the hydrosilylation of allyl alcohol on amorphous hydride silica. We spectroscopically characterized the surface structure of the reaction product and then compared its adsorption behavior with that of the unmodified silica gel and the hydride silica intermediate using selected bases as test solutes. Our interest in evaluating the prediction described above is twofold. First, the preparation of an alcohol-modified intermediate is important for our ongoing efforts to immobilize polymerization initiators onto silica substrates. There is a growing interest in the availability of such materials to carry out surface-initiated living polymerization procedures. Second, preparation of the propanol-bonded silica is a natural extension of our previous work on heterogeneous hydrosilylation [1–6]. To the best of our knowledge, the preparation of such material has never been reported.

2 Materials and methods

2.1 Instrumentation

IR spectroscopy of unmodified, hydride and propanol bonded silicas was carried out using a Shimadzu, Model FTIR-8400 spectrometer (Columbia, MD, U.S.) equipped with a diffuse reflectance IR Fourier transform accessory. Solid state NMR characterization was carried out on the 3-hydroxypropyl bonded silica phase using a Bruker Advance II-400 MHz NMR spectrometer (Rheinstetten, Germany) equipped with a Bruker MAS II probe. Electrophoretic separations were performed on an Agilent model 7100 CE System (Palo Alto, CA, U.S.). Static contact angle measurements were carried out on a home-made goniometer. Carbon content of the modified silica microparticles were determined on a FlashEA 1112 elemental analyzer Thermo Inc. (Waltham, MA, U.S.).

2.2 Materials

Fused-silica capillaries of 50 μm id were purchased from Biotag Inc. (Silver Springs, MD, U.S.) or Polymicro Technologies (Phoenix, AZ, U.S.). UV-grade fused-silica wafers ($25.4 \times 9.0 \times 1$ mm) were purchased from Laser Optex Inc. (Beijing, China). Silica microparticles (NucleosilTM, 7- μm diameter and $91.0\text{-m}^2/\text{g}$ surface area, and YMC GelTM, 10- μm diameter and $287\text{-m}^2/\text{g}$ surface area) were obtained from Macherey-Nagel (Düren, Germany) and YMC Co. (Kioto, Japan) respectively. Piperazine-N,N'-bis(3-propanesulfonic acid) (PIPPS) was purchased from GFS Chemicals (Columbus, OH, U.S.). Allyl alcohol, tris(2,2'-bipyridine) ruthenium(II) chloride, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst, ~2 % Pt in xylene), 2,5-di-tert-butylhydroquinone, triethoxysilane (TES) and DMSO were purchased from Sigma-Aldrich (St. Louis, MO, U.S.). Analytical grade solvents were obtained from various vendors. They were freshly distilled from sodium shavings before use.

2.3 Surface modification

Previous to modification, fused-silica capillaries and wafers were conditioned by treating sequentially with 1 M NaOH at room temperature for 2 h, water for 20 min, 1:1 v/v HCl at 90°C for 1 h and water for 30 min, according to procedures previously reported [15]. Porous silica particles did not undergo any conditioning. All silica substrates were dried at 110°C under N₂ for at least 4 h. Hydride silica intermediates were prepared as described elsewhere [16]. Briefly, 28 μL of a 1.8 mM HCl solution were added to 5 mL of 100 mM TES in THF. After 30 min of magnetic stirring 100 μL of this hydrolyzing solution were added to 9.9 mL of freshly distilled dry cyclohexane and the resulting solution was immediately passed through a 6-m length of capillary tube for 90 min at room temperature (23 ± 2 °C). After this time a total of 10–12 column volumes were collected. In the case of wafers, these were simply immersed in the cyclohexane solution with gentle magnetic stirring. For porous silica, 500 mg of the native substrate were suspended in 31.5 mL of cyclohexane and 3.5 mL of hydrolyzing solution (containing molar ratios of TES, H₂O and HCl with respect to the available SiOH equal to 1.25, 2.5 and 0.083, respectively) were added dropwise over a 30-min time. Then, the mix was allowed to react for 60 min at room temperature. All hydride silicas were cleaned up with THF and dried under N₂ at 110 °C for at least 2 h.

In a typical hydrosilylation on silica particles, 5 mL of a toluene solution being 2.0 M in allyl alcohol, 0.25 mM in the Karstedt's catalyst and 5000 ppm in 2,5-di-tert-butylhydroquinone (as a free radical inhibitor) were heated to about 60–70 °C while being agitated magnetically for about 30 min (a clear solution was obtained immediately after mixing). A 500-mg sample of dry hydride silica substrate was then slowly added to the solution and the reaction was allowed to proceed for 24 h at $85 \pm 1^\circ\text{C}$. The mixture was then centrifuged and the solid washed with three 3-mL portions of toluene followed by similar washings with THF. After the solvent was removed, the solid was dried at 110 °C overnight. Hydride silicas in the form of wafers and capillaries were treated under the same conditions, except that wafers were immersed in the reagent solution under gentle magnetic stirring, while the same solution was forced, by means of applied pressure (typically, 1 bar of N_2), to continuously pass through a 6-m length of capillary (at a flow rate of 1.2 columns per hour).

2.4 Spectroscopy and contact angles

IR, solid state NMR and water contact angles were obtained accordingly to previously described procedures [16].

2.5 Surface coverage

The concentration, Γ_R , of surface-bonded R-groups on porous silica was obtained from the carbon content of the bonded material along with the specific surface area of the hydride intermediate substrate [17].

2.6 CE experiments

Prior to use, capillaries were conditioned with the electrolyte solution (25 mM PIPPS, pH 4.00 ± 0.02) under high pressure (7 bar) for 60 min, after which a stable electroosmotic mobility value was obtained [15]. Electroosmosis determinations followed a method previously described [18].

3 Results and discussion

3.1 IR and NMR spectroscopy

Besides the expected addition of the Si–H bond to the terminal olefin (C-silylation), hydrosilylation of allyl alcohol on the silica hydride may also lead to the formation of an Si–O–C linkage (O-silylation)[13,14]:

(1)

The appearance of strong IR stretching bands in the $3000\text{--}2850\text{ cm}^{-1}$ region, which is indicative of aliphatic C–H symmetric and asymmetric stretching, concomitant with a substantial decline of the Si–H stretching band at 2250 cm^{-1} clearly confirms chemical

bonding to the silica surface, as shown in Figure SI-1 of the Supporting Information. More notably, evidence that allyl alcohol has coupled to the SiH group mostly through C-silylation can be found in the ^{13}C CP-MAS NMR spectrum of the bonded silica phase. The spectrum of Figure 1 shows very intense absorption peaks in the 0–70 ppm range. These absorptions can be assigned to C(1) to C(3) as depicted in the figure. Very weak absorptions at about 113 and 135 ppm are consistent with the terminal and middle olefin carbons, respectively, that remained after some O-silylation. Peak integration reveals that about 94% of the process occurs through C-silylation, as predicted by the reported hydrosilylation by cubic silsesquioxanes $\text{Q}_8\text{M}_8^{\text{H}}$ and T_8H_8 to yield almost exclusively the C-silylation product [13,14]. Noteworthy, besides the β -adduct (3-hydroxypropyl) shown above, C-silylation may also lead to the formation of the α -adduct 1-methyl-2-hydroxyethyl bonded silica after hydrosilylation, but no evidence by NMR spectroscopy was observed for such isomer.

3.2 Bonded phase coverage

A typical plot of 3-hydroxypropyl (propanol) surface coverage, Γ_{PrOH} , as a function of reaction time at $85 \pm 1^\circ\text{C}$ is shown in Figure 2. As expected, most of the alcohol attachment takes place during the early phase of the reaction, while at longer times becomes progressively less pronounced. Figure 2 also indicates an increase in propanol group coverage with decreasing surface area (*i.e.*, increasing pore size) of the silica microparticles, as expected [19]. It seems clear that very high propanol coverage, roughly $5 \pm 1 \mu\text{mol}/\text{m}^2$, is readily obtained after only 12 h of reaction. Since the irregular porous structure of silica microparticles hinders the accessibility of reagents to the active silica sites during surface modification, even higher group densities should be obtained on flat silica surfaces such as those of fused-silica capillaries and wafers where such constrain is virtually absent. Surface coverage is also dependent on the temperature of reaction, as illustrated by the IR spectra in Figure SI-2 of the Supporting Information, where it is evident that the aliphatic C–H stretching band increases as temperature increases and at the expense of the Si–H stretching band intensity. While this result suggests the use of higher reaction temperatures to obtain maximum surface coverage, the highest tolerable temperature is limited in practice by the thermal stabilities of the olefin –which may polymerize– and, particularly, the catalyst –which may be reduced to Pt(0). Whereas some polymerization of allyl alcohol on the silica surface can be tolerated (its thermal radical polymerization may generate additional alcohol groups along with the main backbone structure)[20], darkening of the product was appreciable for a 24-h hydrosilylation at 95°C and became more pronounced with longer reaction times, a feature that has been associated with catalyst deactivation [2].

3.3 Hydrophilicity of propanol-modified silica and related materials

The wettability of the propanol silica surface was assessed by measuring water contact angles on wafers. Table 1 compares the contact angle on the surface of silica wafers at different stages of modification. As expected, the hydride-modified wafer has the greatest contact angle. The lower polarity of the propyl alcohol species on the modified silica, compared to that of the silanol groups on the unmodified substrate, accounts for the decreased hydrophilic character of the bonded silica. As shown in Table 1, upon contact with a 25-mM PIPPS pH-4 buffer solution, the previously hydrided surface loses its hydrophobicity down to a level roughly comparable of that of the unmodified silica. To

further consolidate this observation, hydride silica microparticles were exposed to the same buffer, and IR spectra were taken before and after such exposure. As shown in Figure SI-3 of the Supporting Information, the intense Si–H stretching band of the hydride silica is almost gone upon exposure to the aqueous buffer solution. These observations confirm our previous report according to which exposure of hydride silica wafers to aqueous solutions flattens its contact angle [16]. Such findings are consistent with the intrinsically poor hydrolytic stability of the SiH species along with the complete absence of any protective group on the unbonded hydride silica surface.

3.4 CE characterization of propanol-modified capillaries

The time position and shape of a solute band in an electropherogram depend not only on the electrophoretic mobility of the compound and the electroosmotic mobility of the electrolyte, but also on the solute adsorption equilibrium between the capillary surface and the aqueous electrolyte. Although at pH 4 only a fraction of the silanols present on the inner wall of a fused-silica tube is ionized, the residual electroosmosis may still be used to indirectly assess the extent of surface modification. Data of Table 1 indicate that, under these conditions and in spite of the high propanol group coverage achieved, the PrOH-modified tube shows an electroosmotic mobility level comparable to that of the unmodified capillary (treated only with strong base and acid). Interestingly, while the later tube has a significantly larger population of silanols compared to the PrOH-modified one, its unmodified HCl-treated surface exhibits less ionization at pH 4, as previously reported elsewhere [15]. On the other hand, the hydride capillary, or rather what is left of it after 1-hour exposure to the buffer (recall that such exposure renders the hydride surface hydrolyzed, as described in the previous section) shows a 140% increase in electroosmosis, referred to the unmodified capillary. Since most of the SiH groups of the hydride silica surface are hydrolytically degraded to SiOH, one would expect an electroosmotic mobility level in the hydrolyzed hydride that approaches that of the unmodified capillary. However, related to the later, the increased electroosmotic mobility figure for the hydrolyzed hydride capillary in Table 1 indicates that the regenerated silanols are ionized to a greater degree. The same applies to the hydrolyzed SiH species underlying the immobilized moieties of the PrOH-modified tube. Likely, the short length and hydrophilic character of the anchored propanol chains provide poor protection on the underlying SiH species.

The effect of the surface chemistry of the modified capillaries on the migration behavior of pyridine and caffeine was investigated next. Pyridine ($pK_a = 5.18$) is positively charged at pH 4 and should be susceptible to ion exchange interactions with ionized silanol groups, whereas caffeine ($pK_a = 0.61$), a strong hydrogen bonding acceptor, is uncharged and should bind to the hydrogen of a silanol group. As shown in Figure 3, very similar migration times are exhibited by pyridine on the three capillary surfaces while caffeine shows a great variation in migration. In order to achieve a more meaningful comparison of pyridine and caffeine migration on the different silica surfaces, an electroosmosis-based correction was applied on migration data. As shown in the inset of Figure 3, the essentially identical electrophoretic velocities of pyridine on the three capillaries are not consistent with the corresponding levels of electroosmosis. Since the positively charged pyridine should bind to ionized silanols mainly through an ion-exchange mechanism, the virtual absence of this kind

of surface interaction can be attributed to the high hydrophilicity of this solute (pyridine is water soluble in all proportions) that gives to it a great affinity for the aqueous electrolyte solution. Unlike pyridine, a positive charge on caffeine is very unlikely at pH 4 and this solute may bind to the silica surface predominantly via hydrogen-bond interactions, an effect which would retard its migration towards the cathode. On the contrary, caffeine essentially moves with the corresponding electroosmosis, as evidenced by the fact (not shown) that it co-migrates with the DMSO neutral marker, independently of the surface nature of the tube. While caffeine has a rather moderate water solubility, it does not seem to interact at all with any of the three different silica surfaces. Strictly speaking, however, this means that caffeine does not behave significantly different from DMSO with respect to interactions with the silica surfaces under consideration. It is remarkable, though, that none of the three surfaces under study exhibit any important interaction towards pyridine or caffeine. This is also evidenced by the asymmetry values for their CE bands very close to unity (data not shown).

In order to further explore the adsorptive characteristics of these materials, two stronger silanol-sensitive compounds, $\text{Ru}(\text{bpy})_3^{2+}$ and lysozyme, were used to probe the different silica surfaces and thus comparatively assess their ability to interact. While the doubly positive charge of the Ru complex makes it susceptible to strong cation exchange interactions, lysozyme is a much more complex molecular probe that exhibits correspondingly intricate interactions (cationic and anionic exchange, hydrogen bonding, hydrophobic, van der Waals, etc.) with solid surfaces. Migration time and peak asymmetry of each probe band were measured. Figure 4 shows the band shape for these two probes as a function of concentration and inner-wall surface chemistry. Note that all solute peaks exhibit tailing, the effect being much stronger for lysozyme. Decreasing $\text{Ru}(\text{bpy})_3^{2+}$ concentration reduces the effect: it lengthens the time of migration and slightly decreases the tailing (see also the left upper panel of Figure 5), indicating a non-linear isotherm effect (solute overloading) as previously reported for this probe on LC bonded phases [21,22] and CE tubes [15]. While the lysozyme zones exhibit also unsymmetrical bands with extended tails, under similar conditions they tend to migrate more rapidly as sample load decreases (right panel of Figure 4). Moreover, contrarily to the $\text{Ru}(\text{bpy})_3^{2+}$ complex, decreasing lysozyme load clearly increases tailing (see right upper panel of Figure 5), suggesting not only that a slow adsorption-desorption factor is involved but also that such kinetic effect surpassed that of solute overloading, if at all. This behavior, described profusely elsewhere, is characteristic of compact high pI proteins such as lysozyme [23,24]. Notice also that the extent of this effect is very notorious in the case of PrOH-modified capillaries. Clearly, in spite of the steric protection provided by the dense propanol moieties, a strong interaction with lysozyme is still present. It is likely that such interaction is caused by the presence of remaining SiH groups which were hydrolyzed and resulted in additional active sites. Interestingly, the migration time corrected peak area vs. concentration curve for both solutes on the PrOH-modified material approaches that of the hydrolyzed hydride phase (see lower panel of Figure 5). This result indicates that the unmodified silica material is more likely to contain strong adsorption sites. It seems evident, again, that the hydrolyzed hydride is significantly different from the unmodified substrate with regard to silanol-related interactions, in consistency with water contact angle and electroosmosis results.

3.5 Silica hydride stability, a subject of controversy

Our findings described above appear to exacerbate the ongoing controversy surrounding the stability of the SiH species on silica substrates. For instance, based on a Langmuirian model applied to adsorption isotherm data, Guiochon and his research group arrived at the conclusion that most of the residual Si–H bonds underneath a commercial Cogent™ C₁₈ phase were readily hydrolyzed in contact with aqueous-organic mobile phases (~ neutral pH) and the resulting silanol groups exhibited strong adsorption toward basic solutes [25]. These results seem to contradict those of Jandera and coworkers who, based on linear structure-energy relationship and Langmuirian models, apparently assumed long-term stability of various hydride-based bonded silicas in a number of water-rich mobile phases (pH 3.2 and at elevated temperatures) to explain the retention behavior of selected polar solutes [26–28]. Watson *et al.* reported on the chromatographic behavior of various polar metabolites on a Cogent Diamond™ hydride column in aqueous-organic mobile phases (pH 6.5) and concluded –without explicitly referring to the hydrolytic stability of the LC phase– that the hydride material differs on its chromatographic performance from bare silica [29]. Our own results (see Figure SI-3 and related text) contradict those of Pesek and Matyska who claim that the SiH moieties in a silica hydride column can endure the exposure to water pumped through for several hours without hydrolyzing [30]. One possible explanation to their results may lie on the fact that surface hydrophobicity is controlled by both surface roughness and chemical composition. These two effects are operational in porous hydride silica microparticles and may preclude an effective wetting of the inner particle surface. To circumvent this problem, we added some THF (acetonitrile, dioxane and the like may work as well) to the aqueous buffer to promote wetting and hence an efficient hydrolysis of the SiH groups on silica microparticles.

Although silica surface structure (porous *vs.* flat) imposes certain kinetic differences, the fundamental chemistry of the surface species is essentially the same and, unless proven otherwise, a silicon hydride should behave as such. It seems most probable that unprotected SiH moieties on the unmodified hydride surface easily undergo hydrolytic degradation in aqueous solutions, particularly at alkaline pH. It also appears that the hydrolytic stability of the SiH species beneath a bonded material based on silica hydride (*i.e.*, prepared by hydrosilylation) should be dependent on the degree of shielding provided by the immobilized groups as well as the conditions (particularly pH) used to test stability.

Models may be very useful to understand the retention behavior of solutes in chromatography, but good data fitting to a given retention model is not compelling proof of the mechanism upon consideration. What we report here is very solid evidence that does not rely on theoretical models. IR spectra before and after aqueous buffer exposure of the porous hydride are very straightforward evidence of SiH hydrolytic degradation. The effect is somewhat more pronounced at pHs higher than 4. The substantially decreased hydrophobicity (as measured by water contact angles) of a hydride silica wafer exposed to the same buffer is clear-cut evidence that something very drastic occurs during water exposure. The most likely explanation is that most of the less polar species, SiH, are gone and replaced by more polar ones, SiOH. The high electroosmotic mobility of the hydride CE tube after 1-h exposure to the buffer is indirect but simple to interpret evidence of SiH

degradation to SiOH. Where else do the negative charges responsible for electroosmosis come from?

In the case of a water-exposed unmodified silica hydride, the SiOH groups resulting from the hydrolytic decomposition of surface SiH species (which do not come from the silica support but from the TES reagent) may be more closely packed –in virtue of the minimal steric hindrance of the tiny hydride precursor– and hence interact with solutes in a fashion which is different from that of the unmodified surface. This presumed closeness of the resulting silanol species might explain the unique separation performance exhibited by commercial Diamond™ hydride LC phases. Unfortunately, an unambiguous assessment of such behavior is not possible given the lack of structural information of these phases from manufacturing companies, because the preparation method is regarded as a trade secret. It seems clear, however, that the water-exposed hydride material behaves very differently from the bare silica. But this is not proof that the intrinsically labile SiH groups survive water exposure. Neither is the fact that satisfactory aqueous normal phase separations can be achieved with the hydride phases; usefulness is not proof of hydrolytic stability. Even though we based our conclusions on a single hydride preparation method applied on a limited number of silica substrates, experimental evidence from this work, including water contact angles, IR spectroscopy and CE, is consistent with the anticipated poor hydrolytic stability of the SiH moiety on unmodified hydride silicas. More work seems to be needed to resolve this controversy.

3.6 Potential applications of propanol-modified silicas

We have successfully used the propanol-modified silica as an intermediate material for the preparation –via esterification– of silica-anchored initiators for controlled radical polymerization. The resulting phase consists of active immobilized initiator moieties dispersed over a dense matrix of inactive propanol groups. Such work will be the subject of a new report soon.

Other possible applications of the propanol-bonded phase include the normal phase mode of CEC and LC, also known as hydrophilic interaction liquid chromatography, HILIC. Very symmetric bands similar to those of Figure 3 should be readily obtained for a variety of polar compounds. Additionally, given the small size and high surface coverage of the immobilized propanol groups, the hydrosilylation of allyl alcohol on hydride-based LC phases may be useful as an alternate end-capping procedure.

4 Concluding remarks

The hydrosilylation of allyl alcohol on amorphous hydride silica produces 3-hydroxypropyl bonded phases with a high yield ($\sim 5 \mu\text{mol}/\text{m}^2$). Most importantly, the successful regio-selective (C-silylation) immobilization of propanol groups on silica substrates further confirms the suitability of the growing conception regarding the rigid cage-like silsesquioxane structure as a model for amorphous silica. The validity of our hypothesis that the regio-selectivity predicted from the hydrosilylation of allyl alcohol with cubic silsesquioxanes is also exhibited by the same reaction on amorphous hydride silica was confirmed. CE studies on several silanol-sensitive solutes reveal that moderate to strong ion-

exchange interactions prevail on the propanol-modified phases. A comparative assessment of the new phase vs. unmodified and hydride-modified capillaries confirms that the SiH moieties on the later as well as those remaining amid the propanol-chain network readily hydrolyze upon contact with the aqueous electrolyte solutions commonly used in CE.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

This work was supported by the National Institute of General Medical Sciences of the National Institutes of Health under Award No. R01GM089759, and Universidad del Valle under Project No. CI-7832. The content is solely the responsibility of the authors and does not necessarily represent the official views of the supporters.

Abbreviations

PIPPS	piperazine-N,N'-bis(3-propanesulfonic acid)
TES	triethoxysilane

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Figure 1.
¹³C CP-MAS NMR spectrum of the hydrosilylation product of allyl alcohol with hydride silica microparticles (YMC™).

Figure 2. Effect of reaction time on 3-hydroxypropyl surface coverage (Γ_{PrOH}) for the hydrosilylation of allyl alcohol on hydride silica microparticles. (A) NucleosilTM (91.0 m^2/g). (B) YMCTM (287 m^2/g).

Figure 3.

Typical electropherograms of pyridine and caffeine (late peak) on (A) unmodified, (B) hydrolyzed hydride, and (C) PrOH-modified capillary tubes. All capillaries were from a single lot, with 35.0-cm total length, 26.5-cm effective length and 50- μ m id for dimensions. They were conditioned with the electrolyte solution (25 mM PIPPS pH 4.03 buffer) for 1 h at 7 bar. CE conditions: hydrodynamic injection (3 s at 50 mbar) of 4 mM pyridine and 2 mM caffeine mixture in electrolyte, 28.0-kV voltage applied (18 μ A), detection at 215 nm, 1-min electrolyte rinse between runs. Inset shows electroosmosis-corrected band velocities

for each solute (correction was made by subtracting the electroosmotic velocity from the apparent solute velocity). Electroosmotic velocity is also included as a reference.

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Figure 4.

Effect of solute concentration on migration and band shape of Ru(bpy)_3^{2+} complex (left panel) and lysozyme (right panel) on (A) unmodified, (B) hydrolyzed hydride, and (C) PrOH-modified capillaries from a single lot. Capillary dimensions as in Figure 3. CE conditions: hydrodynamic injection (3 s at 50 mbar) of 20–100 μM Ru(bpy)_3^{2+} and 0.2–1.0 mg/mL lysozyme in electrolyte solution, 14.0-kV voltage applied (9.7 μA), detection at 286 nm (Ru(bpy)_3^{2+}) or 210 nm (lysozyme), 1-min electrolyte rinse between runs.

Lysozyme

Figure 5.

Effect of solute concentration on peak asymmetry and time-corrected peak area for Ru(bpy)_3^{2+} complex (left panel) and lysozyme (right panel) on (A) unmodified, (B) rehydroxylated hydride, and (C) PrOH-modified capillaries. CE tubes and conditions as described in Figure 4. Correction was made by dividing the peak area of each solute by its migration time.

Table 1

Comparative effect of chemical surface modification on water contact angle (WCA) and electroosmotic mobility (EOM) for fused-silica wafers and capillaries, respectively.

silica substrate	WCA $\pm$ SD (n = 3) on wafers, degrees	EOM $\pm$ SD (n = 3) of capillaries ^a $\times 10^{-8}$, $\text{m}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$
unmodified	35 ± 8	0.57 ± 0.01
hydride	60 ± 2	–
hydrolyzed hydride	40 ± 7^b	1.38 ± 0.06
PrOH-modified	45 ± 1	0.67 ± 0.04

^a Capillary tubes (35.0-cm total length, 26.5-cm effective length, 50- μm id) from same lot were conditioned with 25 mM PIPPS pH 4 buffer for 1 h at 7 bar. CE conditions: hydrodynamic injection (3 s at 50 mbar) of 10 mM DMSO in the electrolyte solution as neutral marker, 28.0-kV voltage applied (18 μA) for 5.0 min, hydrodynamic mobilization at 50 mbar, detection at 215 nm, 1-min electrolyte rinse between runs.

^b A hydride-modified wafer was treated with the same buffer containing 1% v/v THF for 1 h with gentle stirring.