

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/277530236>

A new approach for the preparation of a hydride-modified substrate used as an intermediate in the synthesis of surface-bonded materials

ARTICLE in ANALYTICAL CHEMISTRY · MARCH 1993

Impact Factor: 5.64 · DOI: 10.1021/ac00054a027

CITATIONS

93

READS

17

5 AUTHORS, INCLUDING:



Joseph J. Pesek

San Jose State University

321 PUBLICATIONS 4,030 CITATIONS

SEE PROFILE



Junior E Sandoval

Universidad del Valle (Colombia)

15 PUBLICATIONS 619 CITATIONS

SEE PROFILE

A New Approach for the Preparation of a Hydride-Modified Substrate Used as an Intermediate in the Synthesis of Surface-Bonded Materials

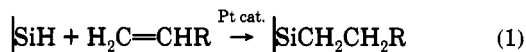
Chao-Hau Chu, Elisabet Jonsson,[†] Mirva Auvinen,[†] Joseph J. Pesek, and Junior E. Sandoval*

Department of Chemistry, San Jose State University, San Jose, California 95192

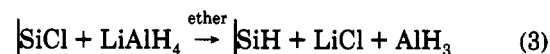
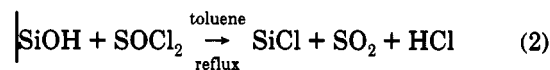
A new approach to produce a hydride-modified support which serves as an intermediate for the synthesis of chromatographic bonded phases is investigated. The procedure, referred to as "silanization", involves the controlled deposition of the hydrolysis product of triethoxysilane (TES) or related silanes to preferentially form an Si-H monolayer on inorganic oxide substrates such as silica. Chemical and spectroscopic, as well as thermal, analyses are employed for the characterization of the intermediate. This synthetic route was developed to improve an existing method for producing a surface uniformly covered with active sites required for further modification via SiH addition to terminal olefins. With the new approach the time-consuming processes associated with the previous¹ reported chlorination/reduction procedure are eliminated. In addition to its greater simplicity, silanization with TES provides superior SiH coverages as compared to the previous method. A number of commercially available silica substrates were subjected to an optimum silanization procedure, and the resulting materials were further derivatized with 1-octene in the presence of a platinum catalyst. The octyl-bonded phases obtained were shown to have good ligand density as well as enhanced resistance to phase deterioration as compared to conventional octyldimethylsilyl silicas.

INTRODUCTION

In previous papers¹⁻³ we have reported the use of olefin addition on a hydride-containing surface as an alternate approach to producing Si-C linkages on silica supports. The bonding reaction, known as hydrosilation, involves the catalytic addition of the surface silicon hydride species to a terminal double bond:

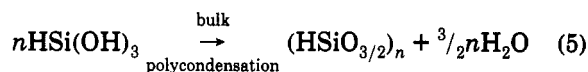


While the feasibility of heterogeneous hydrosilation on hydridized silica substrates has been demonstrated,² the preparation of an intermediate support containing Si-H surface species still constitutes the major bottleneck of the approach as a whole. Hydride derivatization has been carried out by reduction with an inorganic hydride of a silica surface whose silanol groups have been previously converted to SiCl groups¹



A serious limitation of this chlorination/reduction sequence is its extreme sensitivity to moisture during both the chlorination and the reduction steps, resulting in time-consuming, labor-intensive procedures. Additionally, the formation of relatively volatile reduction byproducts requires the use of an efficient condenser (dry ice or equivalent) which further complicates the synthesis.

Two other approaches can be found in the literature for making such a hydride-containing substrate: (i) chemisorption of hydrogen from a pyrolytically activated methylsilica^{4,5} and (ii) the direct preparation of polyhydrosiloxane (PHS) gels having a chemical composition corresponding to $(\text{HSiO}_{3/2})_n$.⁶ The unknown yield of the pyrolysis process along with the high temperature required (about 800 °C) make the use of the former approach less attractive. The PHS gel can be prepared by the polycondensation of the hydrolysis product of a trisubstituted silane in the presence of an inorganic acid catalyst:



where X is a hydrolytically labile group such as halide, alkoxy, acyloxy, etc. Although these PHS gels have been thoroughly characterized,⁷⁻¹¹ the lack of commercial PHS gels hinders the immediate utilization of these materials.

The present report describes a new approach to produce a hydride-derivatized silica for which the synthesis limitations described above are drastically reduced or eliminated. A thorough evaluation of the new hydride intermediate in terms of its spectroscopic, thermal, and chemical properties is reported in addition to comparing it to the product obtained from the sequential chlorination/reduction procedure. The new synthetic approach involves the controlled chemisorption

(4) Morterra, C.; Low, M. J. D. *J. Phys. Chem.* 1969, 73, 321-326.

(5) Morterra, C.; Low, M. J. D. *J. Phys. Chem.* 1969, 73, 327-333.

(6) Budkevich, G. B.; Slinyakova, I. B.; Neimark, I. E. USSR Pat. 215884, 1965.

(7) Slinyakova, I. B.; Budkevich, G. B.; Neimark, I. E. *Kolloidn. Zh.* 1965, 27, 758-764.

(8) Budkevich, G. B.; Slinyakova, I. B.; Neimark, I. E. *Kolloidn. Zh.* 1966, 28, 21-26.

(9) Slinyakova, I. B.; Kurennaya, L. I.; Neimark, I. E. *Fiz.-Khim. Mekh. Liofilnost Dispersnykh Sist.* 1971, No. 2, 313-319.

(10) Budkevich, G. B.; Slinyakova, I. B.; Neimark, I. E.; Zhaigailo, Y. V. *Ukr. Khim. Zh.* 1971, 37, 429-433.

(11) Kurennaya, L. I.; Slinyakova, I. B. *Kolloidn. Zh.* 1975, 37, 178-181.

[†] On leave from The Royal Institute of Technology, Stockholm, Sweden.

(1) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* 1989, 61, 2067-2075.

(2) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* 1991, 63, 2634-2641.

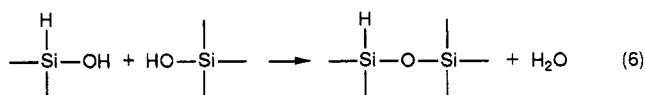
(3) Sandoval, J. E.; Pesek, J. J. U.S. Pat. 5017540, 1991.

Table I. Silica Materials Used in This Work

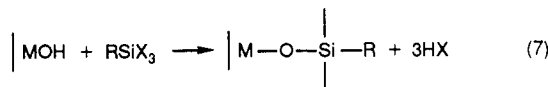
| brand name | particle mean diam, μm^a | pore mean diam, \AA^b | sp surf area, m^2/g^b | silanol content ^c | | maker ^d |
|------------------|--|-----------------------------------|--|------------------------------|----------------------------|--------------------|
| | | | | mmol/g | $\mu\text{mol}/\text{m}^2$ | |
| Partisil-40 | 40 | 90 | 313.5 | 3.32 | 10.5 | 1 |
| Partisil-10 | 10 | 91 | 375.1 | 3.84 | 10.2 | 1 |
| Kromasil-100A | 13 | 104 | 329.1 | 2.16 | 6.6 | 2 |
| Vydac TP (Lot 1) | 10 | 334 | 88.8 | 4.20 | 47.3 | 3 |
| Vydac TP (Lot 2) | 7 | 384 | 94.0 | 4.84 | 51.5 | 3 |
| Nucleosil 300-10 | 10 | 368 | 110.8 | 0.84 | 7.6 | 4 |

^a Data supplied by manufacturer. ^b BET nitrogen adsorption method. ^c From TGA data (110–900 °C weight loss). ^d (1) Whatman, Inc. (Clifton, NJ). (2) Eka Nobel AB (Surte, Sweden). (3) The Separations Group (Hesperia, CA). (4) Macherey-Nagel (Düren, Germany).

of silanetriol, $\text{HSi}(\text{OH})_3$, the hydrolysis product of a trisubstituted silane, on a silica substrate. Hydrolysis (eq 4) is followed by a series of condensation reactions in which the silanetriol is covalently attached to the silica substrate as well as to adjacent silanols (cross-linking) via formation of siloxane linkages similar to those existing in the substrate's framework:



The procedure used can be considered as derived from the so-called "silane coupling" methodology which has been extensively utilized for making surface composites.¹² In silane coupling chemistry, organosilanization of a metal oxide substrate is carried out by reacting an organosilane of the formula RSiX_3 with the inorganic surface:



Normally, the R group contains a terminal reactive functionality which is utilized for ulterior copolymerization with an organic material. The organosilane thus serves as a coupler between the hydrophilic inorganic surface and the organic polymeric material. In our case, the silane reagent will provide active sites for ulterior olefin addition.

Current procedures to make the so-called "polymeric" bonded phases for HPLC involve the same silane coupling reaction (eq 7).^{13,14} This application of organosilanization has prompted extensive studies on the reaction. It has been found that the size of the organic R group strongly determines the extent at which siloxane linkages (M---O---Si) are formed. The "bulkier" the group is, the smaller the extent of condensation and, hence, the greater the tendency to contribute additional silanols to the bonded phase. Within this line of thought, it seems clear that when the bulky organic moiety is replaced by the smallest possible R group, that is, hydrogen, the reaction should proceed with a maximum of siloxane formation. We will refer to this process as just "silanization" to emphasize the replacement of the organic group by hydrogen. In this work, the hydride-modified support is formed by reacting triethoxysilane (TES) with a silica substrate in the presence of water, an acid catalyst, and an appropriate solvent. Certain experimental conditions are required to covalently bind an SiH monolayer by the proposed method. For instance, the initial concentration of silane precursor, TES, must be sufficiently high for surface attach-

ment and cross-linking to occur but must not be so great as to permit bulk polycondensation to proceed to a considerable extent. In the case of a porous substrate such as silica, bulk polymerization of silanetriol may result in a significant decrease of the substrate's pore size, or even to a complete clogging of the porous structure if polycondensation has proceeded too extensively.

EXPERIMENTAL SECTION

Materials. *p*-Dioxane (J. T. Baker Chemical Co., Phillipsburg, NJ) was dried as required by contact with calcium hydride (Sigma Chemical Co., Louis, MO) for several days and then distilled immediately before use. Triethoxysilane and triphenylsilane (Petrarch Systems Silanes & Silicones, Britol, PA) were also used as received. Deionized water was obtained from a Milli-Q water purification system (Millipore Corp. Bedford, MA). The silica materials used and their major physical properties are shown in Table I. They encompass several narrow- as well as wide-pore silicas, most of which are commercially available.

Instrumentation. Differential scanning calorimetric (DSC) and thermogravimetric analysis (TGA) data were obtained by using Perkin-Elmer Models DSC-7 and TGS-2 instruments, respectively, as described in a previous report.¹ A Varian Aerograph Model 204 GC, equipped with a Houston Instrument Omni Scribe chart recorder and a Spectra-Physics integrator, was employed to determine the amount of H_2 gas evolved from a measured amount of hydride-silica sample. Five-milliliter gas-tight syringes (Precision Sampling Corp., Baton Rouge, LO) were used to collect and inject gas samples into the instrument. Carbon analysis on bonded silicas was carried out with a Perkin-Elmer Model 240C elemental analyzer equipped with a Perkin-Elmer Model 56 recorder. Nitrogen isotherms were obtained with a Micromeritics Model ASAP 2400 at Chevron Research and Technology (Richmond, CA). Specific surface areas were measured by the conventional BET method. The adsorption and desorption results were averaged. Mean pore sizes were determined from the adsorption isotherm using the Cranston and Inkley method.¹⁵ Solid-state NMR spectra, cross-polarization (CP) with magic angle spinning (MAS), were acquired on a Bruker MSL 300 spectrometer with a sample of between 200 and 300 mg in a double bearing ZrO_2 rotor. MAS was performed at a spinning rate of 5 kHz. ^{29}Si CP-MAS NMR spectra were recorded with a pulse width of 12 μs using a contact time of 5 ms and a pulse repetition rate of 5 s. All NMR spectra were externally referenced to liquid tetramethylsilane with chemical shifts being given in ppm. Spectral deconvolution for the determination of relative peak areas was done using a standard ("LINESIM") routine provided by Bruker.

PROCEDURES

Silanization. In a typical procedure, a 5.00-g amount of silica was placed in a 3-neck, 100-mL round bottom flask equipped with a condenser, an addition funnel with equalizing tube, a heating mantle, and a magnetic stirrer. A 100-mL amount of dioxane was then added, followed by 7 mL of

(12) Plueddemann, E. P. *Silane Coupling Reagents*; Plenum Press: New York, 1982.

(13) Unger, K. K. *Porous Silica-Its Properties and Use as Support in Column Liquid Chromatography* (Journal of Chromatography Library, Vol. 16); Elsevier Scientific Publishing Co.: New York, 1979.

(14) Sander, L. C.; Wise, S. A. *Anal. Chem.* 1984, 56, 504–510.

(15) Iler, R. K. *The Chemistry of Silica-Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry*; John Wiley & Sons: New York, 1979.

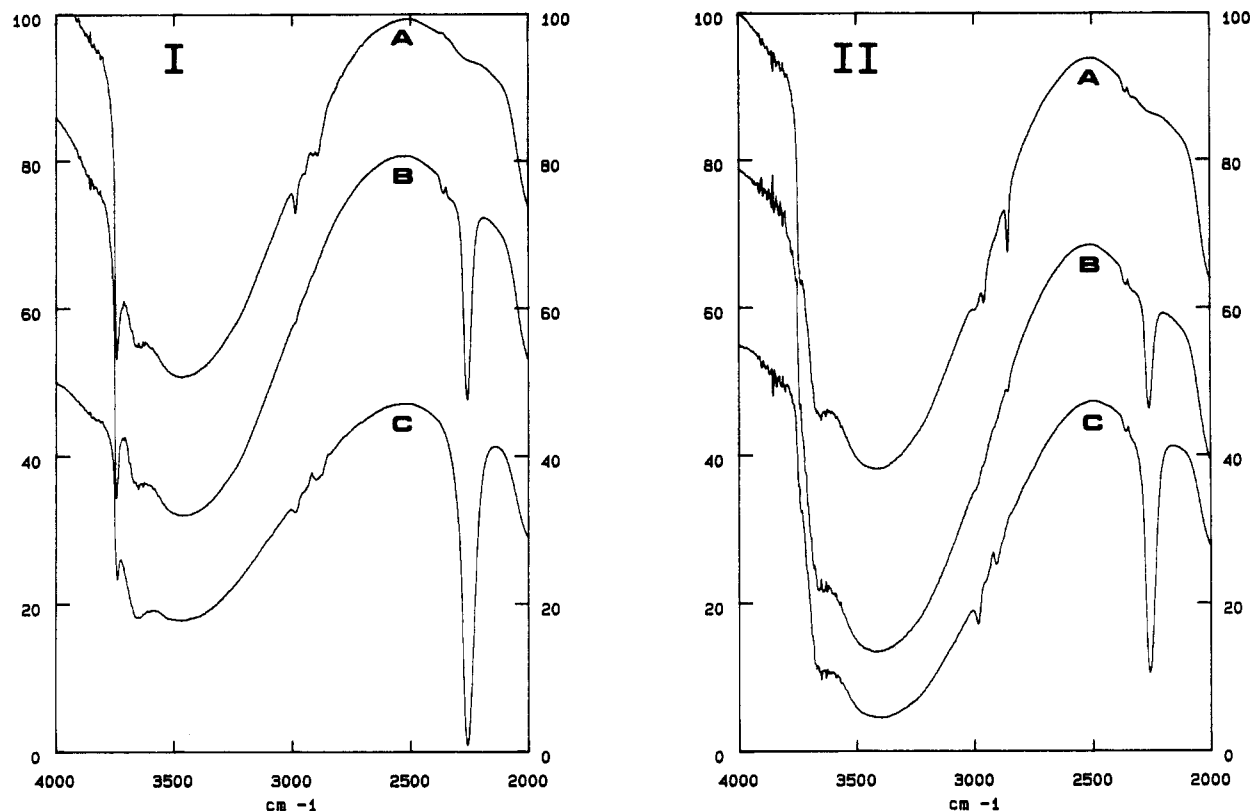
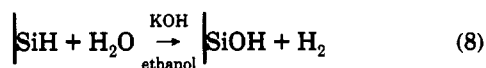


Figure 1. Partial DRIFT spectra of hydride-modified silicas: (I) Partisil-40; (II) Vydac TP (lot 1). Curves: (A) native silica; (B) chlorination/reduction product; (C) TES silanization product. For illustration purposes, all curves were contracted by the same factor and then moved downward. Hence, ordinate units are arbitrary.

(aqueous) 2.3 M HCl solution. The mixture was heated to about 70–80 °C, and then a 45-mL amount of 0.50 M TES/dioxane solution was added dropwise, over a period of 15–20 min. The mixture was then gently refluxed for about 1 h, after which the product was centrifuged and washed consecutively with 50-mL portions of 20:80 water/THF, THF, and diethylether (twice with each solvent). The final product was dried at room temperature and then in a vacuum oven at 110 °C for 6 h or more. For comparison purposes, a chlorination/reduction sequence was applied to the same silica substrate, according to an established procedure.¹ An 18-h chlorination was used in all cases.

Hydride Coverage. The specific SiH content (mmol/g) of the hydride-modified silicas was determined as described by Smith.¹⁶ The method is based on the quantitative generation of H₂ gas from the surface SiH species upon alkaline hydrolysis¹⁷



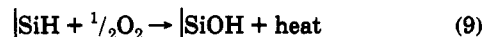
The GC instrument was calibrated against triphenylsilane which was previously standardized by a mercury(II) reduction method.¹⁶ The overall analytical precision of the H₂ displacement/GC (HD/GC) method was about 2–4% relative standard deviation. The observed uncertainty can be attributed mainly to sample handling, particularly during gas collection. The surface concentration of SiH groups (μmol/m²) was calculated from the specific SiH content (mmol/g) and the specific surface area (m²/g) of the substrate.

RESULTS AND DISCUSSION

Preliminary experiments using an alcohol (ethanol) as reaction medium led to the use of an aprotic solvent. Being

a competitive reaction, silanol esterification (alkoxylation) in an alcoholic medium clearly hindered silanol–silanol condensation, particularly at the reflux temperatures required for efficient surface bonding. For this reason, dioxane (bp 101 °C) was used as the solvent. Figure 1 shows partial DRIFT curves for several hydride-modified products. The Si–H stretching band at 2259 cm^{−1} agrees very well with that (2260 cm^{−1}) of a product prepared by a chlorination/reduction sequence.¹ Additionally, a stronger Si–H band clearly suggests a greater silane coverage for the silanization product. Another feature of these spectra is that a band at 3739 cm^{−1} due to O–H stretching of isolated silanols is still present in both hydride-modified products. However, the intensity of this band is smaller for the silanized material. This feature, which was consistently observed on all silicas tested, suggests that the new procedure does not contribute additional (acidic) isolated silanols to the hydrided product. In the case of Vydac TP silicas, this band is hardly visible, even in the native substrate (see panel II of Figure 1). The low population of isolated silanols in this brand of silica has been associated with the low adsorptivity (toward basic solutes) exhibited by bonded phases prepared from it. This chromatographically desirable feature should be preserved or even improved in the corresponding silanized sorbent.

Thermal analysis can also be used to provide further insight into the chemical nature of the silanized material. The thermooxidative degradation of SiH species into SiOH groups is an exothermic process which is accompanied by a mass increase:



These two features can be easily detected by DSC and TGA. Figure 2 shows the DSC curves for several hydride-modified materials. Clearly, the silanized silicas display a stronger DSC oxidation peak, indicating a larger SiH population on these materials. Notice that the position of the peak is about

(16) Smith, A. L. *Analysis of Silicones*; John Wiley & Sons: New York, 1974.

(17) West, R. J. *Am. Chem. Soc.* 1954, 76, 6015–6017.

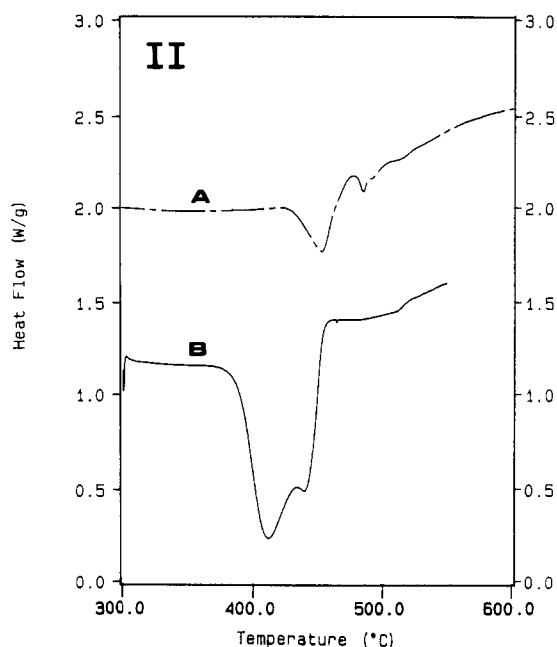
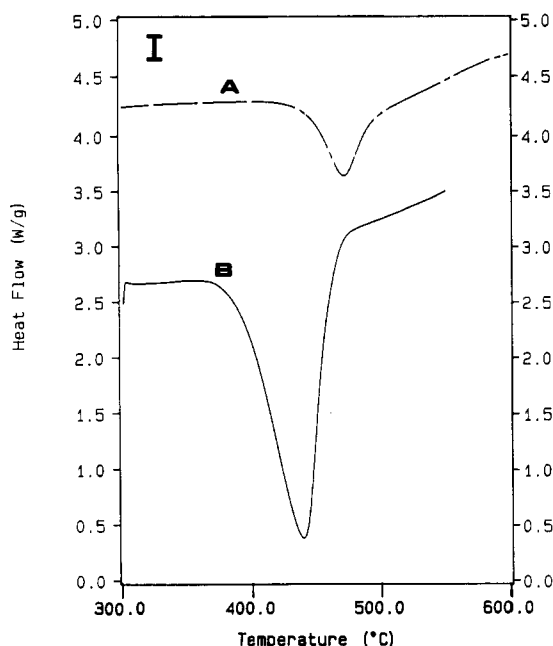


Figure 2. DSC curves for the thermooxidation of hydride-modified silicas in air: (I) Partisl-40; (II) Vydac TP (lot 2). Curves: (A) chlorination/reduction product; (B) TES silanization product.

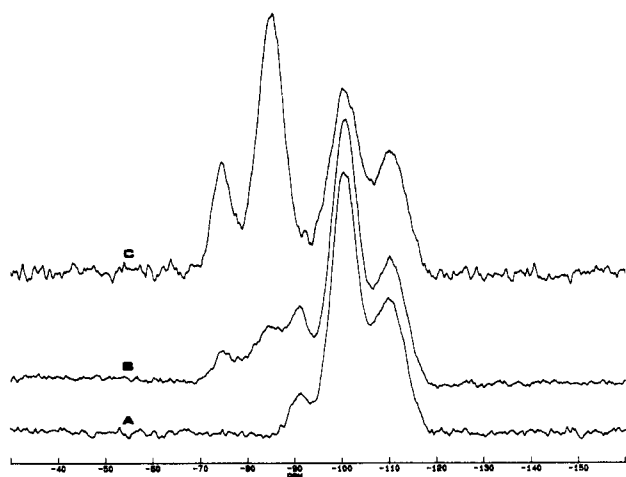


Figure 3. ^{29}Si CP-MAS NMR spectra of Partisl-40 silicas: (A) native silica; (B) chlorination/reduction product; (C) TES silanization product.

20–30 °C lower for the TES-silanized product than that for the “reduced” silica. Additionally, in the case of Vydac silicas, a second oxidation process appears at an even lower temperature (about 410 °C). Such a second oxidation peak is not observed in the case of the corresponding TGA data (not shown).

Another important piece of information is provided by solid-state NMR. Figure 3 shows a comparison of the ^{29}Si CP-MAS NMR spectra for native, “reduced”, and silanized Partisl-40 silica. As expected, there are three peaks in the spectrum of the native silica (curve A) due to siloxanes (Q_4 , $\text{Si}^*(\text{OSi}\equiv)_4$) at -110 ppm, single silanols (Q_3 , $\text{HOSi}^*(\text{OSi}\equiv)_3$) at -100 ppm, and geminal silanols (Q_2 , $(\text{HO})_2\text{Si}^*(\text{OSi}\equiv)_2$) at -90 ppm. When the surface is modified to form a hydride by the chlorination/reduction method, the spectrum (curve B) shows two small peaks at -84 and -74 ppm due to $\text{HSi}^*(\text{OSi}\equiv)_3$ and $\text{HSi}^*(\text{OH})(\text{OSi}\equiv)_2$ moieties, respectively. In contrast, the spectrum (curve C) of the silanized product shows very intense peaks at these positions. It appears that no signal due to $\text{HSi}^*(\text{OH})_2(\text{OSi}\equiv)$ group was shown in any of the NMR spectra.

Similar to other measurements (DRIFT, DSC, and TGA), solid-state NMR data strongly suggest an increase in SiH

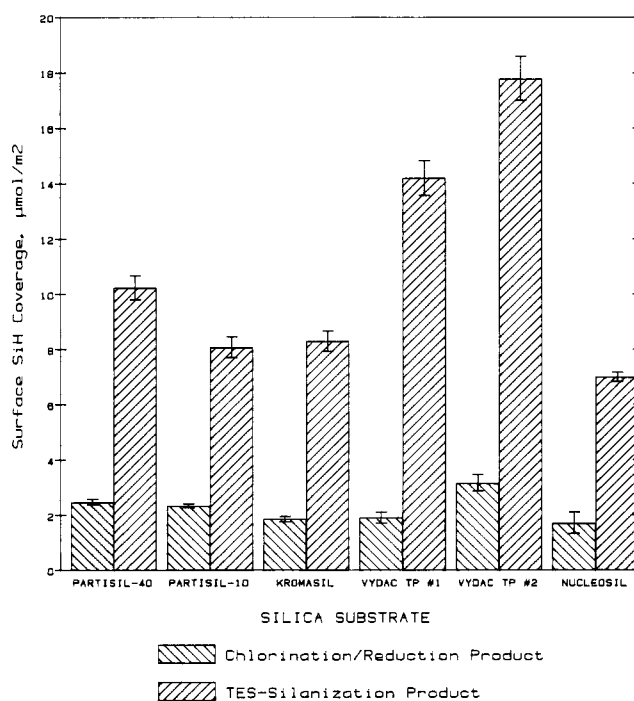


Figure 4. Silane surface density for several commercial silicas subjected to two hydride modification procedures. Error bars reflect the combined uncertainties from HD/GC (specific SiH content) and BET (specific surface area) data.

coverage when silanization with TES replaces the chlorination/reduction sequence. Quantitative determination of SiH carried out by the HD/GC method confirms these observations. This result is shown in Figure 4 for a number of silica substrates. For comparison purposes, the same substrates were subjected to a chlorination/reduction sequence (eqs 2 and 3) according to an established method.¹ It can be seen that roughly a 4–6-fold increase in surface SiH coverage is obtained when the chlorination/reduction sequence is replaced by silanization with TES. The “reduced” products (left-latched bars) as well as the TES-silanized silicas (except the Vydac materials) show a rather constant SiH surface density, the TES product exhibiting an SiH surface density approaching that of SiOH in the corresponding unmodified

Table II. Effect of Hydride Modification on the Mean Pore Diameter (Å) of Several Commercial Silicas

| silica | native material | "reduced" product | silanized product |
|------------------|-----------------|-------------------|-------------------|
| Partisil-40 | 90 | 74 | 76 |
| Partisil-10 | 91 | 94 | 90 |
| Kromasil-100 | 104 | 109 | 106 |
| Vydac TP (lot 1) | 334 | 317 | 278 |
| Vydac TP (lot 2) | 384 | 391 | 344 |
| Nucleosil 300-10 | 368 | 346 | 360 |

substrates. This clearly indicates a high modification efficiency with respect to the starting silanol content. Regarding the Vydac silicas, it should be noted that these materials in their native form exhibit an unusually high silanol content (as measured by weight loss from TGA heating, see Table I). The generally accepted surface density of silanols is about 8 $\mu\text{mol}/\text{m}^2$ for a fully hydroxylated silica.^{13,15} High silanol density on the surface of materials such as Vydac have been attributed to a large population of silanols which are either "buried" or inside extremely narrow channels or micropores.^{15,18,19} Although they are—at least partially—condensed under TGA temperatures (900 °C in our case), these silanols are not accessible to most chemical reagents used for surface derivatization. Additionally, water is very strongly adsorbed in micropores and is known to be retained at temperatures as high as 180 °C.¹⁵ Furthermore, it has been suggested¹⁵ that such microporous substrates cannot be fully accessed by the N_2 adsorbate molecules, and therefore their surfaces are not accurately measured by the BET method. As a result, the number of silanol groups per unit surface area appears abnormally high. The actual reason for a high silanol content in Vydac materials is probably a combination of all of the effects above. Since a large fraction of the total silanol content is not accessible for interaction with the $\text{HSi}(\text{OH})_3$ species, the relatively high SiH coverage for these silicas suggests the formation of some polymeric $(\text{HSiO}_{3/2})_n$ material. An extensive formation of a polymeric layer would result in a corresponding decrease in mean pore size and surface area. Table II shows the effect of hydride modification on the substrate's mean pore size, as determined by the BET N_2 adsorption method. Notice that the Partisil-40 material shows an apparent decrease in mean pore size upon chlorination/reduction. Since this modification necessarily occurs at the surface only, no significant decrease in surface area should be expected. Presumably, the apparent decrease in pore arises either from a relatively large uncertainty in the BET determination or from differences in the interactions between the adsorbate (N_2) and the much more hydrophobic surface resulting from hydride modification. On the other hand, it appears that, within experimental uncertainty, the pore size of the two Vydac materials decreases somewhat as a result of TES silanization, particularly in the case of lot 2. A cursory inspection of the corresponding pore size distribution (PSD) curves (not shown) confirms this observation: a small shift of the curve's maximum in the case of Vydac TP lot 2. Nearly overlapping PSD curves were observed in all the other substrates. It seems therefore reasonable to conclude that, provided a not excessive amount of TES is used, no significant change in the mean pore diameter of the substrate appears to occur as a result of hydride derivatization. Table III shows the effect of hydride modification on the substrate's specific surface area. Simple calculations indicate that for the same silica substrate variability among the three (native, "reduced" and TES-silanized) materials are within the expected pre-

Table III. Effect of Hydride Modification on BET Specific Surface Area (m^2/g) for Several Commercial Silicas

| silica | native material | "reduced" product | silanized product |
|------------------|-----------------|-------------------|-------------------|
| Partisil-40 | 315 \pm 2 | 403 \pm 2 | 349 \pm 2 |
| Partisil-10 | 375 \pm 2 | 417 \pm 9 | 335 \pm 2 |
| Kromasil-100 | 329 \pm 3 | 313 \pm 3 | 275 \pm 2 |
| Vydac TP (lot 1) | 89 \pm 4 | 93 \pm 9 | 83 \pm 2 |
| Vydac TP (lot 2) | 94 \pm 4 | 90 \pm 4 | 92 \pm 4 |
| Nucleosil 300-10 | 111 \pm 3 | 113 \pm 5 | 112 \pm 1 |

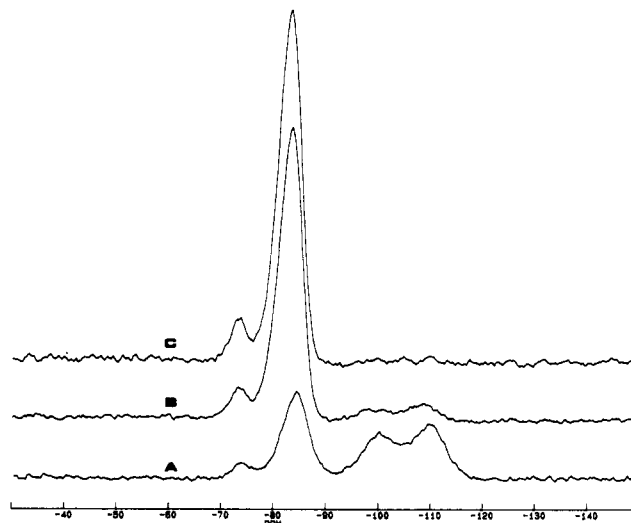


Figure 5. ^{29}Si CP-MAS NMR spectra of hydride materials: (A) silica reacted with 0.1 M TES solution; (B) silica reacted with 2.0 M TES solution; (C) polymeric material produced from a 2.5 M TES solution in the absence of a substrate. Other reaction conditions (HCl concentration, time, etc.) as described in the text. A Vydac HS silica (261 m^2/g ; 104 Å) was used for curves A and B.

cision range for BET-specific surface area (generally between about 1% and 15% relative standard deviation, RSD): below 6% RSD for low-surface silicas and between 9 and 12% RSD for high-surface supports. It would be reasonable to say that, similarly with mean pore size, no significant change in specific surface area occurs as a result of hydride modification.

In order to obtain further information on the nature of the polymeric material which might have been formed on certain substrates, an experiment was performed in which no silica substrate was present and the remaining components were reacted under conditions which promote polycondensation of the silanetriol hydrolysis product (eq 5). The mixture (2.5 M TES in 0.10 M HCl) was allowed to react for about 2 h, and the resulting amorphous polyhydrosiloxane (PHS) material was rinsed with solvent and allowed to dry until a white powdery solid was obtained. The DSC/air curve of this polymeric material (not shown) indicates that the thermooxidative process occurs at a temperature (365 °C) which is substantially lower than that for hydride-modified silicas (430–450 °C). It should be recalled that, in contrast with other silicas which show a single oxidation peak, silanized Vydacs show a second peak at a lower temperature (about 410 °C, see Figure 2). This observation also suggests the formation of some polymeric material on these substrates, under the conditions used. Since the process used to silanize the silica surface can under some conditions lead to polymerization rather than monolayer coverage, it would be useful to be able to distinguish between the two cases by NMR. Figure 5 shows the ^{29}Si MAS-NMR spectrum of a PHS material (no silica) along with those from a lot of Vydac silica which has been subjected to different degrees of silanization with TES. As expected, the PHS material (curve C) shows a major resonance due to fully condensed silanetriol, HSi^* -

(18) Kohler, J.; Chase, D. B.; Farlee, R. D.; Vega, A. J.; Kirkland, J. J. *J. Chromatogr.* 1986, 352, 275–305.

(19) Glajch, J. L.; Kirkland, J. J.; Kohler, J. J. *J. Chromatogr.* 1987, 384, 81–90.

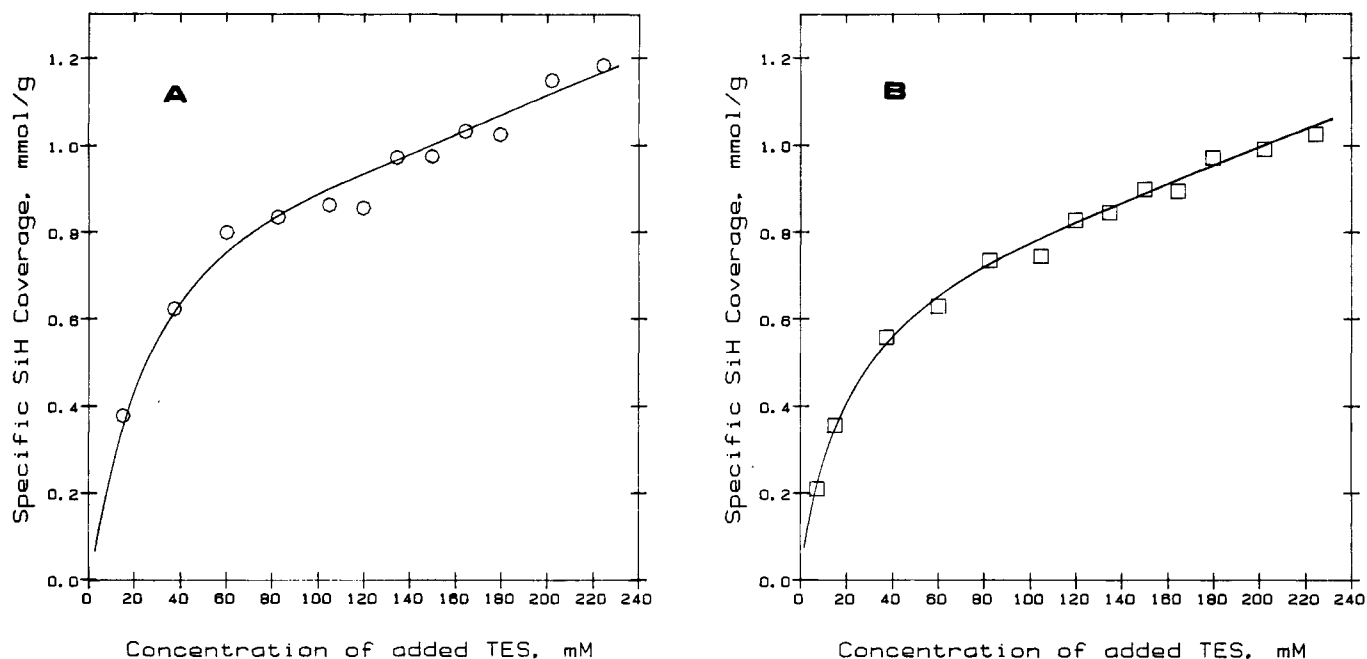


Figure 6. Specific SiH coverage (1-h reaction time) as a function of TES concentration: (A) Vydac TP (lot 2); (B) Nucleosil 300-10.

(OSi≡)₃, along with a weaker signal from partially condensed silanetriol, HSi*(OH)(OSi≡)₂. Predominance of the former clearly indicates a highly efficient silanol condensation, as expected from a minimal steric hindrance from hydrogen in the silane group. Obviously, no Q₄, Q₃, or Q₂ signals are present in the purely polymeric material. Unfortunately, within experimental error, there is no difference in the chemical shift between the polymerized (curves B and C) and the monolayer (curve A) materials. Regarding DRIFT data, a broad and intense absorption due to Si-H stretching is exhibited by the polymeric (HSiO_{3/2})_n products. Similarly with NMR data, no difference in frequency was observed between products obtained under conditions which promote monomeric or polymeric silanization.

Effect of TES Concentration. It appears from the previous section that under certain conditions, particularly those involving high TES concentrations, a polymeric deposit is likely to occur. To examine this effect in more detail, SiH coverage vs TES concentration curves were developed for a number of selected silicas undergoing silanization over a 1-h period. Typical results are shown in Figure 6 for Vydac TP and Nucleosil silicas. Initially, a fast silane chemisorption appears to occur, followed by a much slower reaction. Graphic extrapolation of the second portion of the curve permits one to obtain a rough estimate of the specific SiH coverage corresponding to completion of the initial fast process. After converting to surface area coverages, the estimated "limiting" value for the initial segment of the curve, 8 and 10 μmol/m² for Vydac and Nucleosil silicas, respectively, strongly suggests monolayer formation at TES concentrations of about 110 mM. At this concentration, the coverage by SiH groups approaches 100% of the total silanol groups on the surface (assuming 8–10 μmol/m² for the native silica). This can be rationalized if one recalls that the minimal steric hindrance from the hydride group provides very efficient silanol condensation which rapidly depletes the original substrate's active sites forming a monolayer. Beyond this point (i.e., above 110 mM TES), silanization continues much more slowly, at the expense of a drastically reduced number of uncondensed silanols supplied by hydride-bearing silicons still present (as evidenced by the ²⁹Si NMR resonance at -74 ppm). A further decrease of the silanization rate probably occurs when the multilayer so formed is about to fill the pores of the substrate.

The thermooxidative DSC profiles from this experiment deserve further comment. As shown in panel II of Figure 7, the Vydac TP substrate shows a second oxidation process which appears to start at a TES concentration as low as 40 mM. All remaining silicas under consideration display a single DSC peak which becomes broader and shifts to lower temperatures with increasing TES concentrations (see panel I of Figure 7), probably as a result of multilayer formation. Eventually, a second oxidation peak is developed but at higher TES concentrations. It should also be mentioned that in the case of the Vydac TP supports tested, a high-temperature oxidative process arises when low TES concentrations are used (see curve A of panel II). Similar observations were made when some of these silicas were subjected to a chlorination/reduction process. The singular behavior of Vydac substrates indicates the presence of at least an extra species on these materials, making an interpretation more difficult. As a result of these experiments, a TES concentration of about 110–120 mM was selected and routinely used in further experiments.

Effect of Acid Catalyst. It is a well-known fact that the nature and concentration of the acid catalyst strongly affect the polycondensation as well as the redissolution of silicic acids and its derivatives.^{13,15} Kurennaya and Slinyakova¹¹ have shown that the polycondensation of the hydrolysis product of TES (which produces a PHS gel) accelerates with increasing amounts of the acid catalyst. Very short gelling times were observed by these researchers for concentrations of HCl of 1 M and above. Since we are interested in avoiding gel formation, much lower concentrations were used in our case to obtain a monolayer of silane. Also, the influence of reaction time on silanization was examined by periodically removing a small sample from the reaction mixture. The results, shown in Figure 8, indicate a more rapid and more efficient silane chemisorption with a higher concentration of the acid catalyst, as expected. Under the conditions used, virtually complete coverage is obtained after a few (1–4) hours of reaction.

Suggested Experimental Conditions for the Silanization of Silica with TES. A set of reaction conditions can be derived from the experiments described above. These conditions include (i) use of dioxane as a solvent, (ii) reaction temperature corresponding to a gentle reflux (bp, of dioxane

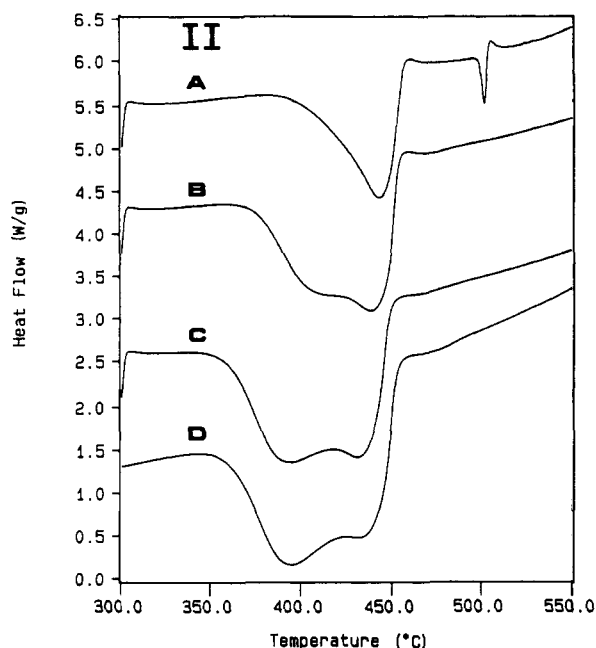
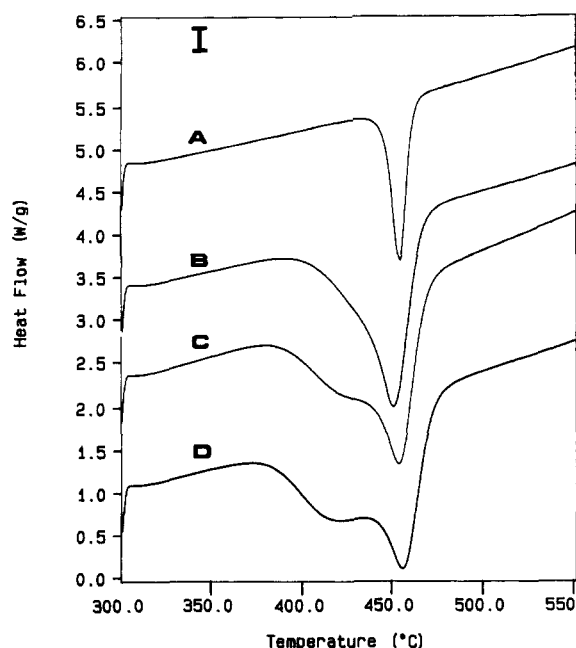


Figure 7. DSC/air thermograms of silanized silicas prepared with increasing TES concentrations. (I) Nucleosil 300: (A) 15 mM; (B) 80 mM; (C) 150 mM; (D) 225 mM. (II) Vydac TP (lot 1): (A) 15 mM; (B) 60 mM; (C) 120 mM; (D) 200 mM.

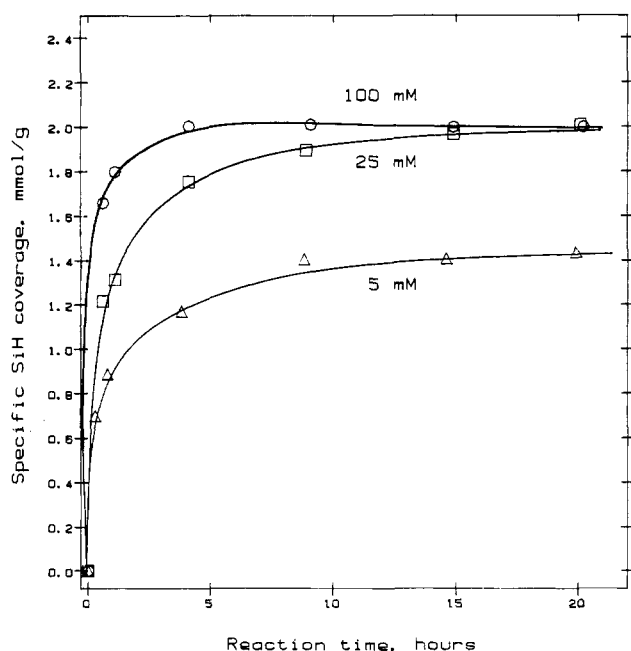


Figure 8. Specific SiH coverage on Vydac TP (lot 2) silica as a function of acid catalyst (HCl) concentration and reaction time. A Vydac HS silica (261 m²/g; 104 Å) was used as substrate.

= 101 °C), (iii) a concentration of HCl catalyst of about 0.1 M, and (iv) a reaction time of 1–2 h. The reaction is carried out by slow (dropwise) but continuous addition of TES/dioxane solution into a silica/dioxane suspension containing an aqueous catalyst solution. Under these conditions, a dense hydrosiloxane monolayer should be formed on the silica surface. Further optimization might be required to systematically minimize the population of uncondensed silanols while maintaining a monolayer of silane species. Precision of SiH coverage for a replicate synthesis under identical conditions was 2.2% ($n = 5$), a value which does not exceed that of the HD/GC method used to determine specific coverage.

Efficiency of Silanization. It was inferred from Figures 4 and 6 that silanization has a high efficiency. Estimated percent efficiencies were calculated from the specific silane coverage, as determined by HD/GC, with respect to the

Table IV. Percent Hydride Modification Efficiencies^a

| silica | chlorination/reduction product | TES silanization product |
|------------------|--------------------------------|--------------------------|
| Partisil-40 | 24 (18) ^b | 97 (59) |
| Partisil-10 | 23 | 79 |
| Kromasil-100 | 28 | 126 |
| Vydac TP (lot 1) | 4 | 30 (43) |
| Vydac TP (lot 2) | 6 | 35 (47) |
| Nucleosil 300-10 | 23 | 92 |

^a Referenced to the available silanols in the starting material.

^b Values in parentheses correspond to percent conversion as determined from ²⁹Si CP-MAS NMR data (see text).

Table V. Surface Coverages of Octyl Silicas Prepared via Hydrosilation with 1-Octene

| silica | corrected ^a % C, by wt | octyl coverage, μmol/m ² | efficiency, % |
|------------------|---|---|---------------|
| Partisil-40 | 9.94 | 3.04 | 30 |
| Partisil-10 | 9.92 | 3.49 | 43 |
| Kromasil-100A | 6.44 | 2.93 | 36 |
| Vydac TP (lot 1) | 2.98 | 3.88 | 27 |
| Vydac TP (lot 2) | 3.31 | 3.90 | 22 |
| Nucleosil 300-10 | 3.47 | 3.37 | 48 |

^a After subtracting the carbon present before bonding.

available silanols on the native silica, as measured by TGA (weight loss between 110 °C and 900 °C). The results are summarized in Table IV. Excluding the Vydac TP silicas, an average $99 \pm 20\%$ efficiency is obtained. It should be noted that the possibility exists that not all the silanols were condensed at 900 °C, and therefore, the SiOH content of some native silicas may have been underestimated. On the other hand, some silicas may contain strongly adsorbed water which could lead to abnormally high surface SiOH densities. Additionally, all silanols may not be truly "available" to condense with silanetriols, as it is known to happen with "buried" silanols.¹⁵ The implication is that the estimated efficiency values shown in Table IV should be interpreted with caution and that strict comparisons are only possible with substrates coming from a single batch of silica.

It should be pointed out that the HD/GC method is a "bulk" one and therefore only measures the total silane content independently from the actual chemical structure of the surface species. To explore the possibility of obtaining quantitative information about silicon sites on silicas from the ^{29}Si NMR data, experimental spectra were compared to simulated curves and the relative areas of the various peaks were calculated. Figure 3 shows that as the hydroxyls are converted to hydride, the intensity of the Q_3 peak decreases with respect to the intensity of the Q_4 peak. These results have been observed previously²⁰ for other types of modifications, and in some cases quantitative evaluations were made.^{18,21,22} Hydride conversion efficiency was measured by simply calculating the relative integrated intensities (areas) of the hydride-bearing silicon species with respect to the sum of all peak areas excluding the siloxane Q_4 .²⁰ As shown in Table IV for some selected samples, it appears that the values calculated from the NMR data do not agree well with those calculated by the gas evolution method. One reason for this discrepancy lies in the obvious fact that the percent conversion from HD/GC data is referred to a highly questionable silanol content obtained from TGA, as mentioned above. The NMR data, on the other hand, only relies on the information from a single experiment. The reason for a relatively low percent conversion can be attributed to the fact that not all the hydroxyl-bearing silicons seen spectroscopically are accessible to the silanetriol reagent. It should be recalled, however, that at present the capabilities of solid-state NMR as a truly quantitative tool are rather limited. Despite this, it seems clear from NMR—as well as IR—data that, although extensive, silanol condensation is not complete. The presence of these remaining silanols may or may not be chromatographically or electrophoretically relevant under common separation conditions. Preliminary experiments in this regard appear to indicate that silanophilic interactions between a TES-silanized silica surface and certain sensitive (basic) probes are virtually absent, as evidenced by chromatographic as well as capillary electrophoretic peak asymmetries very close to unity.

Correlation between H_2 Displacement/GC and DSC/Air Data. It was stated in a previous section that the DSC peak area for the thermooxidation of SiH groups (eq 9) increases with the population of these species on the silica surface. A plot of the DSC/air enthalpy (as measured by the peak area, J/g) versus the specific SiH coverage (mmol/g), shown in Figure 9, clearly indicates that the results obtained with each technique are highly correlated. Obviously, since the HD/GC method does not rely on the measurement of the area of a broad peak such as those commonly obtained by DSC, the former result is more reliable with respect to SiH coverage determination. Nevertheless, the fitted data can be used to obtain a rough estimate of SiH coverage from DSC/air measurements, the latter having the advantage of not requiring any sample manipulation other than loading on the instrument's pan. An intercept statistically higher than zero can be attributed as a contribution to the correlation from tailing DSC/air peaks which tend to give a negatively biased enthalpy measurement. As a consequence, any estimate of SiH coverage from a calibration plot such as that in Figure 9 should be used with caution and, when accuracy is mandatory, must be confirmed by a direct measurement using the HD/GC method.

Bonded Phases from Silanized Silicas. Octyl-bonded silica packings were prepared from the new hydride intermediate by reacting them with 1-octene in the presence of a platinum(II) catalyst as described in a previous work.² Surface coverage data for the bonded silicas are summarized in Table

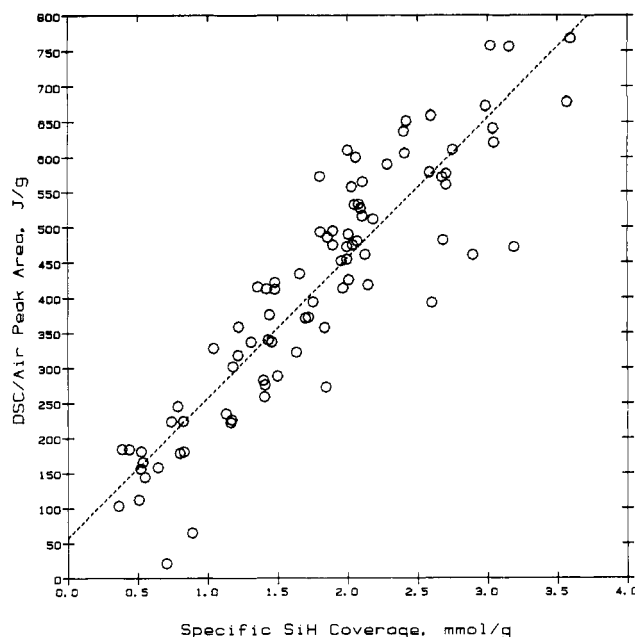


Figure 9. DSC/air peak areas as a function of specific SiH coverage. Linear fitting results: slope = 199 ± 10 J/mmol, intercept = 58 ± 20 J/g, $R^2 = 0.8153$, $n = 87$.

Table VI. Estimated Percent of Silicon Sites for Hydride- and Octyl-Modified Vydac TP (Lot 1) Silica Phases as Measured by ^{29}Si CP-MAS NMR

| species | octyl phase ^a $R = n\text{-C}_8\text{H}_{17}$ | hydride phase $R = \text{H}$ |
|--|---|---------------------------------|
| I $\equiv \text{SiOH}$ (Q_3) | 69.2 | 54.1 |
| II $\equiv \text{Si}(\text{OH})_2$ (Q_2) | 8.7 | 2.7 |
| I + II | 77.9 | 56.8 |
| III $\equiv \text{SiR}$ | 11.2 | 39.9 |
| IV $\equiv \text{Si}(\text{OH})\text{R}$ | 11.0 | 3.3 |
| III + IV | 22.2 | 43.2 |
| % III/(III + IV) | 50.5 | 92.4 |

^a 5.20 $\mu\text{mol}/\text{m}^2$.

V. One of the most important features of this type of bonded phase is its hydrolytic stability, particularly when used with aggressive chromatographic mobile phases. A particularly aggressive eluent is that containing an aqueous solution of trifluoroacetic acid (TFA). It has been shown that a rapid column degradation takes place when these mobile phases are used during the chromatographic separation of proteins.²³ To estimate the extent of phase degradation, selected bonded silica samples were subjected to prolonged exposure to a solution containing 0.1% v/v of TFA as described in a previous report.² Similar to phases prepared from chlorination/reduction hydride intermediates, octyl-bonded materials from TES-silanized intermediates showed an extent of phase deterioration which was significantly lower than that of the same substrate modified by conventional octyldimethylsilanization. Again, these simple long-term hydrolysis experiments clearly demonstrate the superior hydrolytic stability of Si-C linkages as compared to that of Si-O-Si-C linkages present in currently used bonded silicas. More extensive long-term phase degradation tests based on a chromatographic procedure are required to further substantiate the hydrolytic advantage exhibited by the new bonded phases.

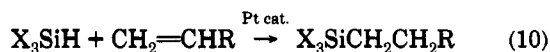
(21) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* 1981, 103, 4263-4265.

(22) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* 1983, 105, 3767-3776.

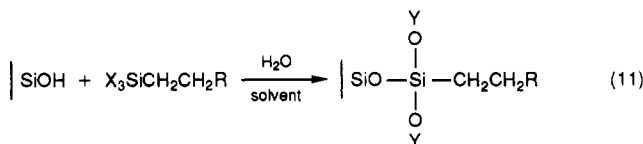
(23) Glajch, J. L.; Kirkland, J. J.; Köhler, J. J. *J. Chromatogr.* 1987, 384, 81-90.

(20) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* 1982, 86, 5208-5219.

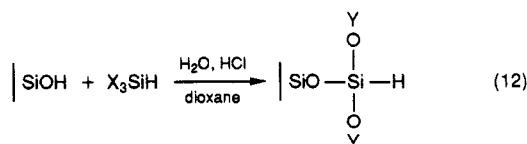
Hydrosilation versus Organosilanization as the Primary Surface Bonding Process. The overall scheme for preparing conventional "polymeric" (alkyl) bonded phases generally involves two steps (end-capping not being considered). First, an organosilane reagent is made by *hydrosilation* in homogeneous phase:



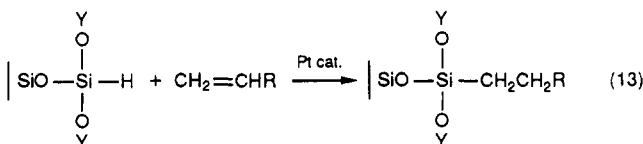
Second, the organic moiety is attached to the substrate by a heterogeneous phase reaction, (*organo*)*silanization*:



Where Y = H or Si≡. Our synthetic route also involves two steps. First, an intermediate is made by heterogeneous *silanization*:



Second, the organic moiety is attached to the hydride-modified substrate by another heterogeneous phase reaction, *hydrosilation*:



The point to be made here goes, however, beyond a simple reversal of the reaction sequence. Since the siloxane linkage, Si-O-Si, and not the Si-C bond is the hydrolytically labile portion of the organosiloxane structure, the important issue becomes which silanization process (eq 11 or 12) renders the stronger surface attachment. Here, a stronger surface attachment refers to one with a higher number of siloxane linkages. Such linkages result from covalent attachment of the silane to the silica surface and from cross-linking between adjacent silanes. It is known from previous studies^{21,22} that in the case of trisubstituted silanes the number of linkages ranges between 1 and 3. In fact, the rationale of this work was based on the greater silanol condensation resulting from the minimal steric hindrance effected by a tiny hydride compared to a bulky alkyl group. Clearly, the process described by eq 12 should provide a greater number of siloxane linkages. ²⁹Si NMR can be used to confirm this expectation, as shown in Table VI. Hydride and "polymeric" octyl phases were prepared from a single batch of Vydac TP silica by respectively using the current method and that described by Sander and Wise.¹⁴ It can be seen that only about half of all octyl-bearing silicon species were fully condensed (via siloxane formation) while more than 92% of the hydride-bearing silicons lost all the hydroxyl groups. Similar measurements on several hydride substrates yield an average 85 ± 6% (n = 7). Additionally, it is evident that the overall conversion efficiency of hydride silanization was greater by a factor of almost 2 when compared with that of octyl silanization, under

the conditions used. Moreover, the fraction of Q₃ + Q₂ species was greater for the octyl phase.

An interesting comment that can be derived from the preceding discussion concerns the intrinsically monomeric bonded phases resulting from the reaction between silica and alkyltrimethylchlorosilanes. These phases show a fairly acceptable hydrolytic stability for many applications, even though only a single siloxane linkage is formed between the surface and the bound species. This relative stability is probably due to the shielding effect provided by the relatively bulky methyl groups. A clear proof for this argument has been already provided by Kirkland et al.²⁴ they found that a considerable increase in hydrolytic stability was achieved when the methyl groups were replaced by bulkier 2-propyl and 2-methyl-2-propyl groups. Perhaps the greater hydrolytic stability shown by some "polymeric" bonded phases lies in the simple fact that they have a larger number of siloxane linkages which make them more difficult to remove via hydrolysis than their monomeric counterparts.

CONCLUSIONS

Generally speaking, the primary goals of this study have been met: compared to the chlorination/reduction sequence, silanization with TES does indeed provide a simpler and more efficient approach for preparing a hydride-modified silica substrate. Under these conditions, TES silanization provides SiH coverage efficiencies of about 100 ± 20% (with respect to available silanols). This represents about a 4-fold improvement over the chlorination/reduction approach.

Besides improving silane coverage, the new procedure effectively eliminates the strictly dry condition required by the chlorination/reduction method. In fact, the presence of water is required to hydrolyze the ethoxy groups of TES into silanols. Furthermore, the potential hazard associated with aluminum hydride byproducts¹ is completely eliminated. As a result, TES silanization is simpler and more economical to carry out than the chlorination/reduction sequence: (i) consumption of reagents and solvents is greatly reduced; (ii) at the bench level, process time is reduced from 3–4 full days to about 4 h; (iii) use of manpower is drastically reduced.

Due to its simplicity, ease of carrying out, enhanced SiH coverage, and freedom from dry conditions, it is clear from the results of this study that silanization with TES should replace the chlorination/reduction as a means to produce hydride-modified silica substrates. The issue of SiH monolayer formation is, however, more difficult to assess. Results from DRIFT, DSC/air, TGA, and HD/GC cannot be used to directly evaluate the extent of an eventual multilayer formation. DRIFT, DSC, and to a lesser extent TGA indirectly evaluate the "purity" of the chemisorbed SiH species. For instance, we attributed the observed broadening of the DSC oxidation peaks to an increasing contribution from polymeric materials of the type (HSiO_{3/2})_n. However, an unequivocal assignment of such species has not been obtained at this point.

Extension of TES silanization to other inorganic oxide substrates is an important application of the procedures described in this work. Porous materials such as alumina, zirconia, and titania, among others, are amenable to being modified with a monolayer of silane. Further modification of the hydride substrate by olefin hydrosilation should provide a variety of separation materials for chromatographic use.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation through Grant No. 9119933 and by The Separations Group.

(24) Kirkland, J. J.; Glajch, J. L.; Farlee, R. D. *Anal. Chem.* 1989, 61, 2–11.