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Synthesis and Characterization of a Hydride-Modified Porous Silica Material as an Intermediate in the Preparation of Chemically Bonded Chromatographic Stationary Phases

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A novel synthetic approach to produce chemically bonded silica-based chromatographic stationary phases is presented and discussed. The procedure involves the preparation of a silica intermediate containing stable silicon hydride (silane) surface species followed by the catalytic addition of these to organic compounds bearing a terminal vinyl group. This paper deals with the preparation of the hydride intermediate via chlorination of silica followed by reduction with lithium tetrahydridoaluminate. Several spectroscopic and thermoanalytical techniques were used to obtain information regarding the structural characteristics of the surface-reduced silica material. It was found that the surface SiH species formed were hydrolytically stable at low pH and thermally stable in the presence of oxygen at temperatures up to about 450 °C. Postreaction treatment of the hydride-derivatized solid with aqueous hydrochloric acid was also found to be essential to remove aluminum byproducts from the silica surface while presumably increasing the extent of silane formation.

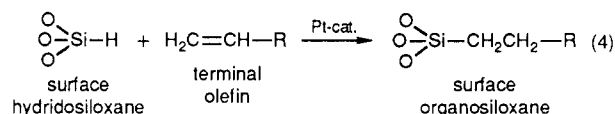
INTRODUCTION

Because of their high versatility and superior selectivity, chemically modified silicas have been used as supports in a wide variety of chromatographic applications. Numerous synthetic procedures have been developed to attach organic moieties (R) onto the silica surface. Reaction of fully hydroxylated silica with triorganochlorosilanes (silanization) to give organosiloxane-type linkages has been the most commonly used approach (1, 2). A vast majority of commercially available bonded phases belong to this category, *n*-octyl- and *n*-octadecyldimethylsilyls being the preferred modifying groups. In another approach, direct Si-R linkages have been formed by sequentially reacting silica with thionyl chloride (SOCl₂) and a proper Grignard (3, 4) or organolithium reagent (5, 6). Based upon steric considerations as well as relative bond strengths in silicon chemistry (7-9), the latter method should provide not only a closer attachment and a denser coverage of organic functionalities onto the silica surface but also a more hydrolytically stable bonded phase than that obtained by the corresponding organosiloxane-type structure. Silanization, however, is by far more popular presumably because of the commercial availability of a variety of silanizing reagents and the relative ease with which the reaction is carried out. It thus seems clear that to replace the currently available silanization technology for making bonded phases, any new approach has to demonstrate greater simplicity of the synthetic procedure, superior coverage of the silica surface, and/or higher hydrolytical stability of the attached groups.

The overall synthetic scheme for silica silanization generally involves several steps, as shown in Figure 1. A prebonding reaction is carried out to prepare the silanizing reagent, usually via catalytic addition of a SiH group to a terminal olefin (hydrosilation). The primary silica derivatization reaction involves the nucleophilic attack of surface silanols at the central silicon atom of the silanizing reagent. Additional silanization of the modified support (end-capping), this time

with trimethylchlorosilane or hexamethyldisilazane, is usually carried out to somewhat reduce the surface concentration of unreacted silanols left by the primary bonding reaction.

A cursory look at the reaction scheme of Figure 1 reveals that by using the prebonding reaction 1, an alternate Si-C bond can be formed directly between the silica surface and the organic group



Since the two bulky methyl groups will no longer be present, this alternate scheme should result in a closer packing of the anchored organic groups as well as a more stable bonded phase. Naturally, the new synthetic strategy would require that (i) silicon hydride (silane) species were already present on the solid support and (ii) the heterogeneous hydrosilation reaction proceeded with a good yield. The latter prerequisite appears to be of immediate importance since without a good yield of the adduct, attempting to synthesize surface SiH species would be pointless. A cursory literature survey in which special attention was paid to the addition of hydridosiloxane (O₃SiH) groups to terminal olefins revealed several important points about what can be expected from olefinic addition with this class of silanes.

The addition of silicon hydrides to alkenes has been recognized as one of the most important laboratory methods to form Si-C bonds. The reaction's minimal interference with other reactive functionalities (e.g.: CO₂R, CN, NH₂, etc.) has permitted the attachment of silicon to organic molecules which otherwise cannot be introduced by regular organometallic procedures (7). Hydrosilation is generally carried out in the presence of a transition-metal catalyst. A variety of inorganic and organic platinum complexes have functioned as very effective catalysts for the addition reaction, chloroplatinic acid in a 2-propanol solution (also known as "Speiers" catalyst) being the most commonly used form. Only as little as 10⁻⁵ mol of platinum/mol of silicon hydride is normally required for an effective hydrosilation (7, 8). The addition is rapid and can be done at room temperature or under reflux to ensure a high yield. The mechanism of the reaction in homogeneous phase has been thoroughly studied and is thought to involve a hexacoordinated platinum intermediate formed by the addition of the Si-H group to the olefin-catalyst complex. Details can be found elsewhere (7, 10).

Indirect evidence for the feasibility of the addition of surface silicon hydride groups to terminal olefins can be obtained from the works by Chalk and Harrod (10) and Musolf and Speier (11). In their reports, organosiloxanes of the type (RO)₃SiH and (R₃SiO)₃SiH (R = CH₃-, C₂H₅-) have been shown to give the adducts at yields above 90%. More recently, and perhaps more relevant, Laub and co-workers (12) have successfully used hydrosilation to attach a variety of mesomorphic (liquid crystal) molecules bearing a terminal vinyl group to the backbone of poly(methylhydridosiloxane) ([OCH₂SiH]_n-) materials. The mesomorphic nature of the polymeric adduct

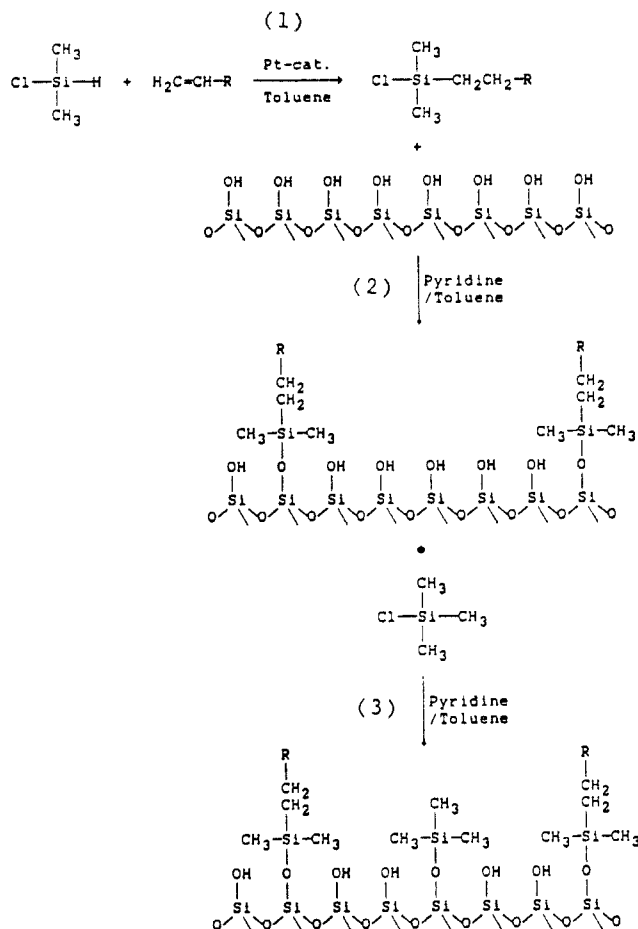


Figure 1. Typical reaction scheme for the silanization of silicas: (1) prebonding reaction (preparation of the silanizing reagent); (2) primary bonding reaction; (3) "end-capping".

when produced in significant yield was probably responsible for its remarkably high selectivity as a stationary phase for the gas chromatographic separations of polycyclic aromatic hydrocarbons. It might therefore be concluded at this point that hydrosilation of terminal olefins onto the surface of a silica-containing SiH species seems to have great potential as an alternate approach for the preparation of chemically bonded chromatographic phases.

With the establishment of the feasibility of the heterogeneous hydrosilation, it is possible to focus on the production of an intermediate silica support bearing silicon hydride as its primary surface species. Two major approaches can be envisioned: (i) chemical derivatization of fully hydroxylated porous silicas and (ii) direct preparation of a porous poly(hydridosiloxane) ($\text{HSiO}_{1.5}$)_n gel. The commercial availability of a variety of silicas with well-characterized geometries along with the relatively simple chemistry involved in its hydride derivatization (see below) make the former approach the first choice. However, it should also be pointed out that procedures similar to those for preparing regular silica have been explored for the preparation of poly(hydridosiloxane) materials. For instance, a xerogel of this kind has been synthesized via hydrolytic polymerization of triethoxysilane (13). The product has been extensively characterized (13-18) and may provide a convenient starting support material for surface hydrosilation of terminal olefins.

Reduction with an inorganic hydride can be conveniently applied to producing SiH groups on the silica surface after converting the SiOH to SiCl groups. Because of its extensive silanol conversion and simplicity, reaction with SOCl_2 in toluene as a solvent is a very common method for chlorinating silica (9). The product has been usually prepared as an in-

termediate for further silica derivatization, for instance, by reaction with organometals to produce Si-alkyl or Si-aryl surface groups. Similarly with other surface modifiers, complete silanol conversion is limited by steric hindrance due to the slightly larger cross-sectional area of a chloride group compared to that of the original hydroxyl (about 0.24 and 0.21 nm², respectively) (9). Because of the good yields (typically >90%) obtained, lithium tetrahydridoaluminate dissolved in an ether solvent is by far the preferred reducing reagent for the preparation of hydroorganosilanes (8). Diethyl ether is usually employed as the solvent but tetrahydrofuran (THF), dioxan, and ethylene glycol dimethyl ether have also been used. Other reducing agents include sodium hydride in a hexamethylphosphoric triamide (HMPT) solution, calcium hydride in the presence of alkylaluminum hydride, and trimethylamine hydrochloride in the presence of magnesium in a HMPT medium (8). The reaction involves the nucleophilic attack of highly polarized hydride species on the silicon atom, via a pentacoordinated intermediate (8, 19). The facile nature of the leaving group, a halide, along with the high strength of the nucleophile, hydride, explain the commonly found high reactivity and elevated yield of the reaction. Similar behavior can therefore be expected from the analogous heterogeneous reduction of chlorinated silica.

Reduction of silica can also be carried out by chemisorption of hydrogen from a pyrolytically activated support, in a fashion similar to that reported by Morterra and Low (20, 21). Formation of surface silane groups was observed when non-porous methoxylated silica (Aerosil) was pyrolyzed under vacuum at about 750 °C (20). Subsequent hydrogen-treatment of the 830 °C pyrolysis product led to the extensive formation of Si-H species, as evidenced by IR spectroscopy (21). Although a quantitative evaluation of the extent of surface reduction was not attempted, IR data also showed that a significant amount of silanol groups were also present in the hydrogenated silica. Yet, this material was found to be strongly hydrophobic and to exhibit good stability on the presence of oxygen and water vapor at temperatures up to 350 and 400 °C, respectively. Not surprisingly, these observations are consistent with those from poly(hydridosiloxane) xerogels (17).

It should be pointed out that this behavior contrasts with that of simple organohydrosilanes ($\text{R}_{4-n}\text{SiH}_n$, $n = 1-3$, R = alkyl) which are sensitive to hydrolytic cleavage, particularly in alkaline media (22, 23). The observed stability of silicon hydride species in silica, however, should not be entirely surprising especially if one considers the similarly high chemical and thermal stability of polymeric siloxanes. In siloxane chemistry (7, 8) it has been widely accepted that the stability of these compounds is largely due to the decreased Si-H bond polarization which results from the multiple ($p \rightarrow d$)_π backbonding between the oxygen free electron pair and the empty d orbital of the silicon atom. An obvious consequence of the high stability is that it makes surface-reduced silica a very convenient synthesis intermediate which can be handled under fairly regular laboratory conditions. In contrast, highly reactive intermediates such as chlorinated silica in a Grignard synthesis will always require carefully controlled conditions to avoid their degradation into undesirable products.

The general purpose of this work was to investigate the feasibility of bonding organic moieties to silica supports via the heterogeneous hydrosilation of terminal olefins with surface silicon hydride species. The overall synthetic procedure involves two major steps: (1) Preparation of a chemically and thermally stable silica intermediate in which the original surface silanol groups are replaced by silicon hydride species; and (2) attachment of organic functionalities containing a

terminal vinyl group via addition with the surface hydrides. In this paper we report the results obtained from the preparation of such an intermediate, accomplished by chlorination of silica followed by reduction of the silicon chloride groups to their corresponding hydrides. Diffuse reflectance infrared Fourier transform (DRIFT) spectrometry, ^{29}Si cross-polarization magic angle spinning nuclear magnetic resonance (^{29}Si -CP-MAS-NMR), and electron spectrometry for chemical analysis (ESCA) were used to obtain information about the chemical nature of the reduced silica surface. Thermoanalytical techniques such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were also used to further characterize the new hydride-derivatized material.

EXPERIMENTAL SECTION

Materials. Toluene and diethyl ether (EM Industries, Inc.) were dried by allowing them to stand with calcium hydride (Sigma Chemical Co.) for several days, refluxing, and then distilling from the hydride immediately before use (24). A 0.2 M lithium tetrahydridoaluminate (Sigma Chemical Co.) ether solution was prepared and used as the reducing reagent. Thionyl chloride (Gold Label, Aldrich Chemical Co.) was used as received. IR-quality potassium bromide (Harshaw/Filtrol Partnership) powder was used for the FT-IR spectra. Partisil-40 (Whatman, Inc., Clifton, NJ) with a 40- μm mean particle size, 85- \AA mean pore size, and 350 m^2/g surface area (manufacturer's typical data) was used as the silica material.

Spectrometry. DRIFT spectra were taken in the 4000–450- cm^{-1} region with a Perkin-Elmer Model 1800 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. A Spectra-Tech DRIFT accessory equipped with a 13-mm diameter, 2-mm depth sample cup was used. KBr was ground in an agate mortar and dried in an oven at 120 $^{\circ}\text{C}$ for at least 24 h. After cooling down, the KBr matrix was mixed with an equal amount (by weight) of silica material and finally kept overnight in a vacuum desiccator at room temperature. Samples were filled into the DRIFT accessory's cup with gentle tapping until a small sample mound was formed. A very smooth sample surface was then obtained by pressing down a microscope slide onto the cup while moving it in a circular motion. Before a spectrum was obtained the height of the sample cup was adjusted by using the alignment routine provided with the standard Perkin-Elmer software. This resulted in a reproducible positioning of the sample surface at the optimum height so that a maximum signal throughput was consistently obtained. Spectra were collected at a nominal resolution of 2 cm^{-1} with a weak Norton-Beer apodization. Two hundred sample scans were ratioed against pure KBr as reference. Wavenumbers corresponding to maximum absorption were assigned by utilizing a "peak" routine provided with the instrument's standard software. Band intensities (absorbance units) for triplicate DRIFT spectra of samples prepared in this manner had a relative standard deviation equal to or better than 7%. Spectra shown were normalized to 100% transmittance.

^{29}Si -CP-MAS-NMR spectra were obtained at Catalytica Corp. (Mountain View, CA) on a Bruker MSL-400 NMR spectrometer at 79.5 MHz. The cross-polarization time used in all experiments was 5 ms with an MAS rate of 5 kHz. The recycle time was 10 s and typically 2000 scans were required to obtain a good signal to noise ratio. External TMS was used as a chemical shift reference.

ESCA measurements were done at Surface Science Laboratories (Mountain View, CA) with a Surface Science Laboratories Model SSX-01 spectrometer equipped with an Al K α X-ray excitation source. Spectra were obtained at an energy resolution of about 1 eV from a 600 \times 1000 μm sample spot. Typically, the X-ray beam penetrated the top ~ 100 \AA of selected silica samples.

TGA measurements were carried out at Lockheed Missile & Space Company, Inc. (Sunnyvale, CA), with a Perkin-Elmer Model TGS-2 analyzer equipped with uncovered alumina crucibles. Typically 30 mg of selected silica samples were loaded in the analyzer, heated to 110 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$. and held at this temperature until deflection of the weight signal was no longer detected. The temperature was then raised at the same rate up to 1000 $^{\circ}\text{C}$ and again held at this value until no further weight loss could be detected.

DSC experiments were performed with a Perkin-Elmer Model DSC-7 instrument. Uncovered platinum pans loaded with about 10-mg silica samples were subjected to the same heating cycle described above for TGA measurements, with the final temperature being 700 $^{\circ}\text{C}$. Both DSC and TGA experiments were performed under oxidizing (air) as well as inert (N_2) atmospheres.

Silica Derivatization. All reactions were carried out under a dry N_2 atmosphere in glassware that had been previously dried at 120 $^{\circ}\text{C}$ overnight. The LiAlH_4 ether solution was prepared in a N_2 -flushed glovebag. Transfer of liquids was carried out either with a glass syringe (<20 mL) or by means of a stainless steel cannula and N_2 pressure, via silicone rubber septa (25). Prior to reaction, the silica was dried under vacuum at 120 $^{\circ}\text{C}$ overnight and then cooled in a vacuum desiccator.

Chlorination of Silica. A 5.00-g portion (approximately 14 mmol of silanol, assuming 4.6 groups/ nm^2) of dried silica was suspended in 60 mL of freshly distilled, dry toluene, and 10.2 mL of thionyl chloride (about a 10-fold molar ratio excess with respect to silanol content) was added. The mixture was magnetically agitated and the chlorination was allowed to proceed under reflux for at least 48 h, after which the excess SOCl_2 was distilled off. Removal of any remaining SOCl_2 was carried out by washing the dark purple product at least 8 times with 30-mL portions of dry toluene while magnetically stirring for 15 min. After each washing, and once the solid had settled, the solvent was carefully aspirated off to waste by means of a vacuum applied to a glass pipet. Finally, the chlorinated silica was washed with one 30-mL portion of dry diethyl ether, remaining in a final fresh ether aliquot.

Reduction of Chlorinated Silica. A 70-mL portion of 0.2 M LiAlH_4 ether solution (about a 4-fold molar ratio, hydride:original silanol) was added *slowly* to the chlorinated silica/ether suspension. An immediate reaction was evidenced by a color change from dark purple to white. The reaction was allowed to proceed for 2 h under a gentle reflux. A dry-ice condenser was found to be appropriate to safely condense relatively volatile intermediate reduction byproducts, namely $\text{AlH}_n\text{Cl}_{3-n}$ ($n = 1$ to 3). The excess of LiAlH_4 was carefully aspirated off and destroyed by adding dry ethyl acetate (about 10 mL) followed by 2-propanol dropwise with stirring until hydrogen evolution ceased (26). This also confirmed that an excess of the reducing reagent was present at the end of the reduction reaction. The product was next washed as described above with eight 30-mL portions of dry ether to remove any remaining aluminum hydride and/or chloride species in solution. The "reduced silica" was then dried overnight in a vacuum oven at 120 $^{\circ}\text{C}$.

Hydrolytic Stability Tests. A suspension consisting of 10 mL of test solution (0.01 M NaOH, water, or 0.1 M HCl) per gram of selected reduced silica is magnetically agitated at room temperature for 60 min (or as otherwise specified). The solid is then filtered through a glass fritted funnel, washed with several portions of deionized water, then ether, and finally dried under vacuum at 120 $^{\circ}\text{C}$ overnight.

RESULTS AND DISCUSSION

DRIFT Data. The Si-H group is readily identified by a strong stretching band in the range 2300–2100 cm^{-1} , along with a relatively weak bending band between 760 and 910 cm^{-1} (27), the former being located in a region where the absorption due to the silica matrix is minimal. When chlorinated silica was reduced with an excess of LiAlH_4 , a broad peak was produced at about 2280–2200 cm^{-1} . The shape of the peak suggested a multiplet whose resolution could be enhanced by applying a spectral deconvolution routine (Perkin-Elmer's standard software), as shown in Figure 2. The position of the composite band is consistent with that of SiH species in which the silicon atom is bonded to several electronegative atoms (20, 21, 27, 28). Although the multiplet may be attributed to more than one possible SiH species (namely $\equiv\text{SiH}$ and $\equiv\text{Si}(\text{OH})\text{H}$ which originated from single and geminal silanols respectively), the formation of surface AlH (alane) species, which is also feasible under the reaction conditions, may also explain at least partially the low-frequency component of the broad absorption. Due to the excess of reducing reagent, the presence of unreacted silanols, and the virtual absence of shielding effect

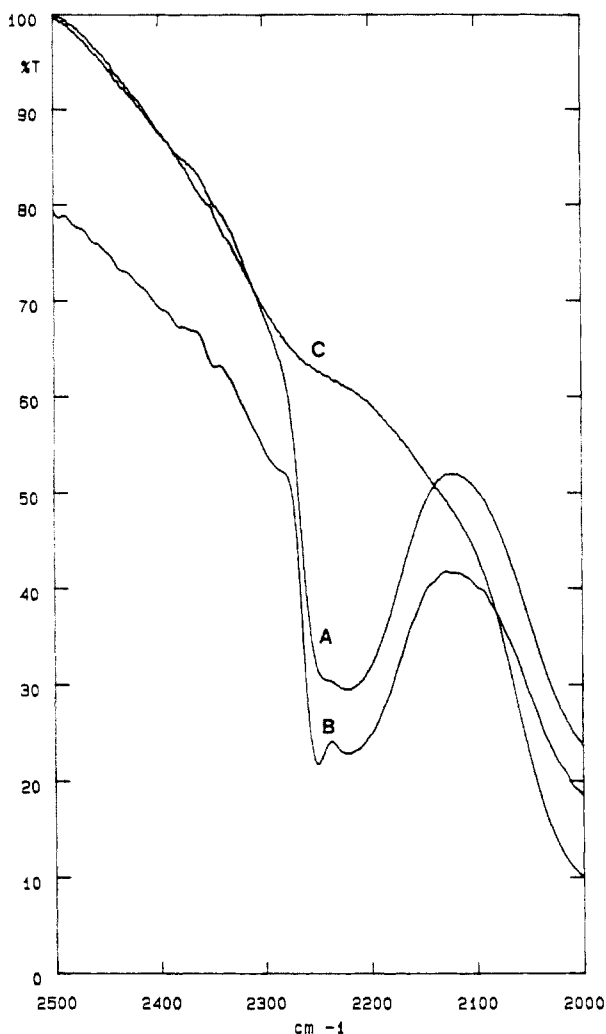
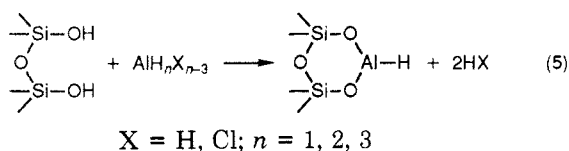


Figure 2. Partial DRIFT spectrum of reduced silica: (A) chlorinated silica reacted with excess LiAlH_4 ; (B) curve A after spectral deconvolution, a doublet at 2250 and 2222 cm^{-1} is strongly suggested; (C) unreacted (fully hydroxylated) silica. Curve B has been displaced downward for better illustration.

from hydrogen atoms as the reduction of chlorinated silica progresses, the silanols become increasingly accessible to attack by the reducing reagent, leading to the formation of surface alane species



This situation is contrary to that of most (if not all) silica derivatizations, in which the original surface species become progressively inaccessible to the modifier's attack. Indirect as well as direct evidence support our hypothesis that surface alane species are formed during the late stages of reduction: (i) Reactions similar to that described above have been shown to occur between fully hydroxylated silica and other Lewis acids such as aluminum trichloride and hydroborane (9, 29); (ii) the stretching mode of Al—H species is known to occur at somewhat lower wavenumbers (about 1700–1900 cm^{-1} , depending on substitution and extent of solvation) as compared to that of SiH groups (30, 31); and (iii) slow but unequivocal gas evolution ($\text{X} = \text{H}$ in reaction 5) was observed after the reacting mixture was allowed to settle for several minutes and the reaction flask was gently tapped (in fact, gas evolution was more readily observed by using a much larger excess of reducing reagent). To confirm our hypothesis of aluminum

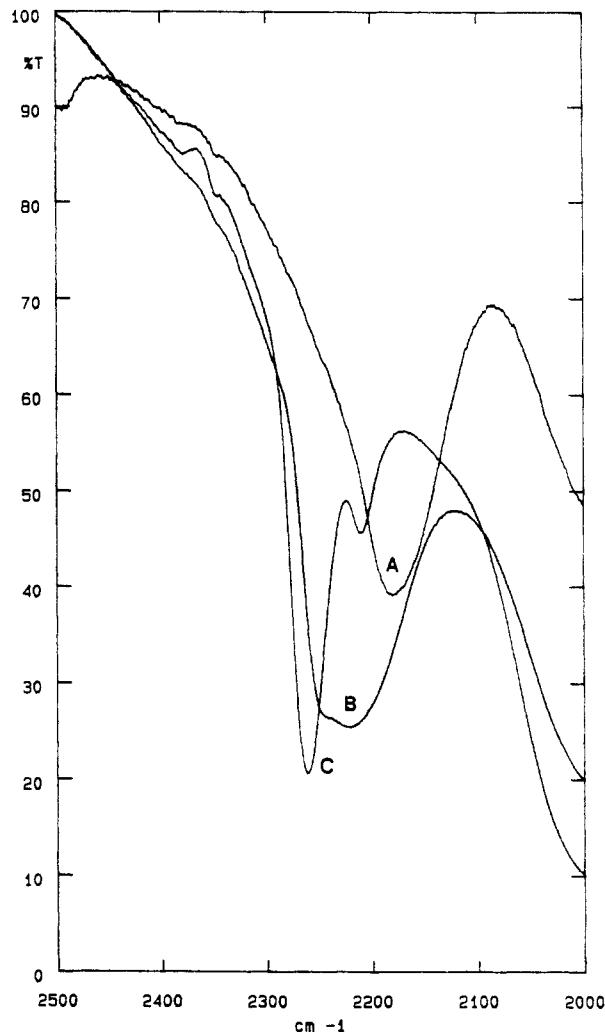


Figure 3. Partial DRIFT spectra of hydride-derivatized silicas: (A) fully hydroxylated silica reacted with LiAlH_4 ; (B) chlorinated silica reacted with excess LiAlH_4 ; (C) chlorinated silica reacted with substoichiometric amount of LiAlH_4 .

chemisorption, a small amount of unreacted (i.e., fully hydroxylated) silica was treated with ethereal LiAlH_4 . A relatively broad and asymmetrical peak at 2181 cm^{-1} , very likely due to surface alane species formed through reaction 5, was obtained. As in the case with silanes, one can expect substitution on the central atom with oxygen-containing groups to cause Al—H stretching frequency shift toward higher values as compared to those for unsubstituted alanes. As clearly shown in Figure 3, surface alane species (curve A) formed as a byproduct during the reduction step are a major contributor to the broad DRIFT absorption observed in reduced silica (curve B). On the other hand, when chlorinated silica was reacted with a *substoichiometric* amount of LiAlH_4 (roughly 1 mequiv of hydride per 3 of original silanol) a major peak at 2262 cm^{-1} along with a small shoulder at 2211 cm^{-1} were produced, as also shown in Figure 3 (curve C). Under these conditions reduction should occur preferentially at the SiCl sites, and therefore the high-frequency component of the original broad peak (curve B) can be reasonably attributed to strongly absorbing $\equiv\text{SiH}$ species. On the other hand, without further experimental evidence, it would be highly speculative to simply assign the 2211- cm^{-1} shoulder to $\equiv\text{Si}(\text{OH})\text{H}$ species.

It is a well-known fact that silica-alumina surfaces are easy to form because of the structural similarities between the two oxides (29, 32). Potential difficulties associated with the presence of chemisorbed aluminum in reduced silica are 2-fold.

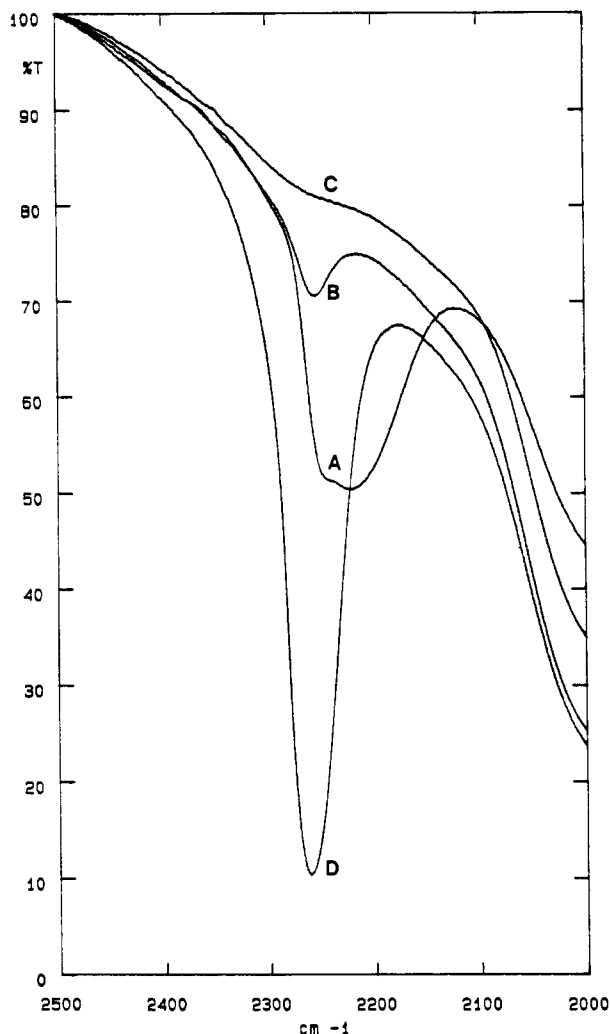


Figure 4. Partial DRIFT spectra showing the effect of hydrolysis on reduced silica: (A) chlorinated silica reacted with excess LiAlH_4 ; (B) product A treated with 0.01 M NaOH for about 2 h; (C) same as B with overnight treatment; (D) product A treated with 0.1 M HCl for about 1 h.

First, alumina-like sites on the silica surface will make the latter more complex, and therefore increasingly difficult to predict and perhaps to derivatize. This appears to be due to the intrinsically more complicated nature of alumina surfaces: multiple aluminol types as well as Lewis-acidity and oxidative capabilities of the alumina sites (29). Second, but perhaps more important, if not removed, surface alane species will reduce a platinum(II) catalyst to the inactive platinum-black form when the reduced silica is used in the subsequent bonding reaction 4 (7, 10, 14). To investigate the hydrolytic stability of silane as well as alane surface species, small portions of reduced silica (chlorinated solid reacted with excess LiAlH_4) were treated with 0.01 M NaOH, deionized water, and 0.1 M HCl. As evidenced from slow gas evolution and confirmed by DRIFT spectra (see Figure 4) treatment with aqueous alkali ($\text{pOH} \sim 2$) resulted in the complete elimination of both alane as well as silane species (curve C) while water ($\text{pOH} \sim 7$) does so at a much slower rate. Acidic ($\text{pOH} \sim 13$) treatment on the other hand resulted in the complete elimination of the low-frequency alane component of the originally broad band and, interestingly, a significant increase in the intensity of the 2260 cm^{-1} Si-H band (curve D). These observations can be readily interpreted in terms of the well-known hydrolytical cleavage of alanes and silanes which results in the formation of silanol and aluminol species, respectively, along with H_2 evolution (8, 13, 30). On the other hand, the observed enhancement of the Si-H band intensity

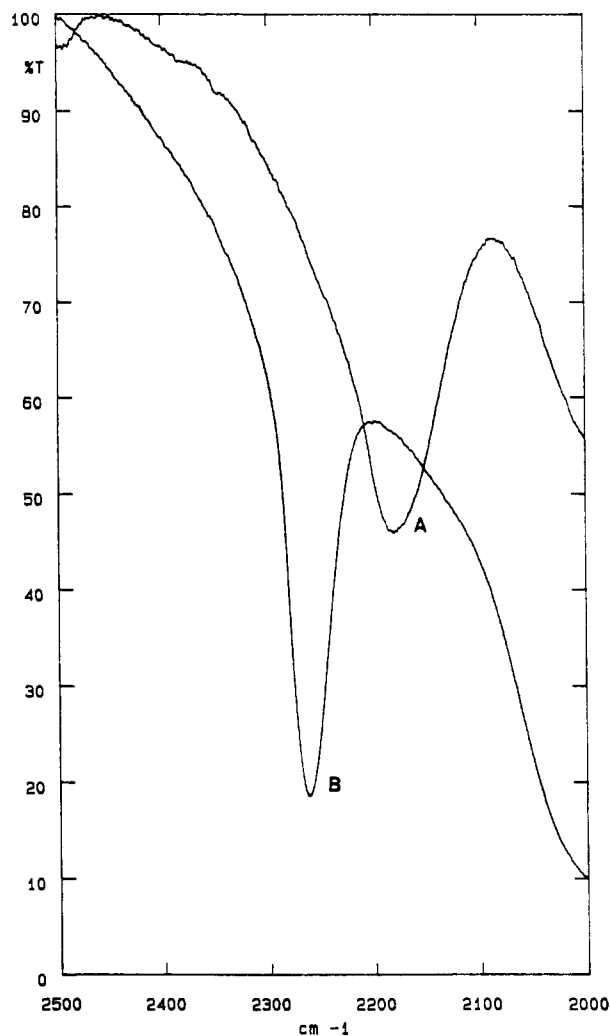


Figure 5. Partial DRIFT spectra showing the effect of hydrolysis on surface alanes: (A) fully hydroxylated silica reacted with LiAlH_4 ; (B) product A treated with 0.1 M HCl.

may be attributed to the effect of either or both of two factors: (i) the hydrolytic removal of IR-active =Al-H species from the silica matrix which may cause an increase of the effective penetration of IR radiation and thus a more intense SiH absorption; and (ii) the formation of additional surface SiH species at the expense of adjacent alanes. While the effect of an absorbing matrix on DRIFT intensity has been documented in a previous work by Brimmer and Griffiths (33), there is a need at this point to further elucidate the role of alane species on the enhanced SiH absorption. Two related hydrolysis experiments were thus carried out in which the following silica derivatives were treated with 0.1 M HCl solution: (i) the product of the reaction between *fully hydroxylated* silica and ethereal LiAlH_4 (containing AlH but no SiH groups); and (ii) the product of the reaction between chlorinated silica and a *substoichiometric* amount of LiAlH_4 (containing SiH groups but virtually no AlH groups). The results are illustrated in Figures 5 and 6, respectively. The former clearly shows the formation of a band at the SiH frequency along with concomitant collapse of the AlH absorption, indicating that silane groups may be formed at the expense of alane species. The fact that product (ii) shows a virtually unchanged SiH band upon acid treatment (Figure 6) is also consistent with this reasoning (i.e., in the absence of AlH species, no additional SiH groups are formed). Figure 7 further illustrates the effect of low-pH hydrolysis on reduced silica: the enhancement of the Si-H stretching band upon acid treatment is also accompanied by reappearance of the free-

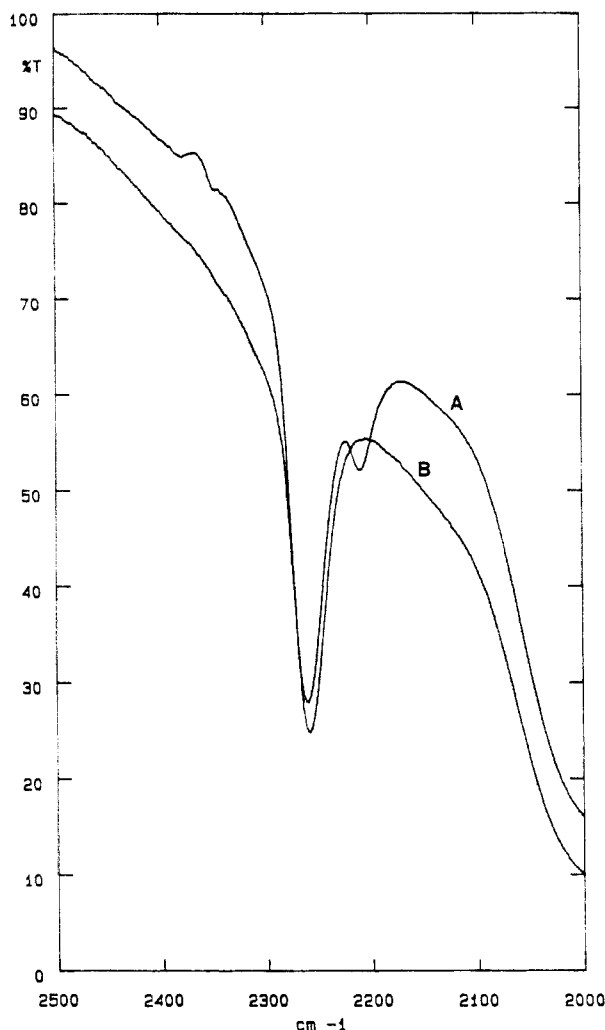


Figure 6. Partial DRIFT spectra showing the effect of hydrolysis on partially reduced silica: (A) chlorinated silica reacted with substoichiometric amount of LiAlH_4 ; (B) product A treated with 0.1 M HCl for about 1 h.

silanol stretching peak at 3739 cm^{-1} . These observations could be accounted for on the basis of a nucleophilic substitution reaction between a surface hydride (alane) species and a protonated siloxane bridge, followed by the hydrolytic removal of the aluminum species, according to the reaction scheme depicted in Figure 8. Protonation of the strained siloxane bridge (a) is postulated here as a means to facilitate its cleavage and thus promote the nucleophilic attack of the neighboring hydride. Additionally, solvation (hydration) of the chemisorbed alane group (b) is likely to occur under these conditions.

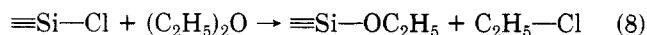
Another interesting point is that the Si-H stretching mode became one of the most prominent bands in the infrared spectral region under consideration, with an intensity which is comparable to those for silanol and water bands (Figure 7, curve B). Finally, it should be mentioned that a weak absorption band at 885 cm^{-1} characteristic of the Si-H bending vibration (17) was also present in the DRIFT spectra of reduced silica. This is depicted in Figure 9 along with the corresponding curve for native silica. Of course, because of the multiple interferences in this region, mainly from Si-O vibrations, the stretching mode is much more useful for characterization purposes.

^{29}Si -CP-MAS-NMR Data. Another potential method for studying the changes in silica surfaces is ^{29}Si -CP-MAS-NMR (34). In order to further substantiate the possible presence of an alane species, several types of modified surfaces were compared. When fully hydroxylated silicas were treated with

LiAlH_4 , a peak near -83 ppm appeared. In general, thorough acid washing could be used to remove this peak. These data support the DRIFT spectra which shows the formation of an additional surface species when silica is reacted with LiAlH_4 or when chlorinated silica is reacted with an excess of LiAlH_4 . This species is then removed upon acid treatment.

ESCA Data. The ESCA technique can produce valuable information about many chemisorbed species present on the reduced silica surface, with the exception of hydrogen. Figure 10 shows partial ESCA spectra of unreacted silica (curve A), along with the reduced material before (curve B) and after (curve C) treatment with aqueous hydrochloric acid. Five consecutive 10-min washings with the acid (10 mL of 0.5 M solution per gram of solid) were carried out to thoroughly eliminate unwanted species present on the surface. Clearly, this procedure efficiently removes chemisorbed aluminum (characterized by two peaks with binding energies of 75 and 116 eV) from the untreated material down to the background levels of unreacted silica. Curve B also shows the presence of chemisorbed chloride (binding energies of 195 and 266 eV), probably in the form of =Al-Cl produced via a process similar to that of reaction 5.

Curiously enough, traces of chemisorbed carbon (binding energy 281 eV) are also significantly removed through acid treatment. This is also observable in Figure 7 in the form of very weak C-H stretching peaks in the $2900\text{--}3000\text{ cm}^{-1}$ region. Carbon chemisorption can be explained in terms of a secondary reaction (solvolysis) taking place during the reduction of chlorinated silica in ethereal medium (7)



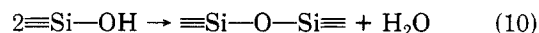
Subsequent removal of the carbonaceous species during acid treatment is consistent with the well-known hydrolytic instability of the Si-O-C linkage (8, 9).

As mentioned before, complete elimination of surface alanes from reduced silica is necessary in order to minimize the deactivation (via reduction) of a Pt(II) catalyst during the surface hydrosilation of terminal olefins. Treatment of the reduced material with aqueous acid must therefore be incorporated as a mandatory step in the synthesis of the silica intermediate.

Thermal Data. The behavior of poly(hydridosiloxanes) and related materials (7, 21) in the presence of oxygen at temperatures above 350°C has been associated with the oxidative degradation of silane species into silanol groups



Since it is an exothermic process which involves a mass increase, oxygen chemisorption on reduced silica can be analyzed by both TGA and DSC. Figure 11 shows that a weight increase in air (curve A) occurs, starting and peaking at about 440 and 530°C , respectively. Clearly, this weight gain peak was superimposed on a loss weight process which started at about 280°C , as indicated by the heating of a similar sample under inert N_2 atmosphere (curve B). This weight loss is due to the well-known silanol condensation process



Due to the opposite effects on sample weight from the simultaneous reactions 9 and 10, the TGA data did not provide a satisfactory measure of the extent of surface reduction. Assuming that the oxidation peak height truly represented the weight gain due to reaction 9, attempts to measure the surface concentration of SiH species only accounted for about 10% of the silanol content in the starting (unreacted) silica material. While this apparently low result might suggest a poor efficiency of the chlorination/reduction reaction sequence, the relatively rapid decline of the TGA oxidation peak indicates the strong possibility that once formed the new

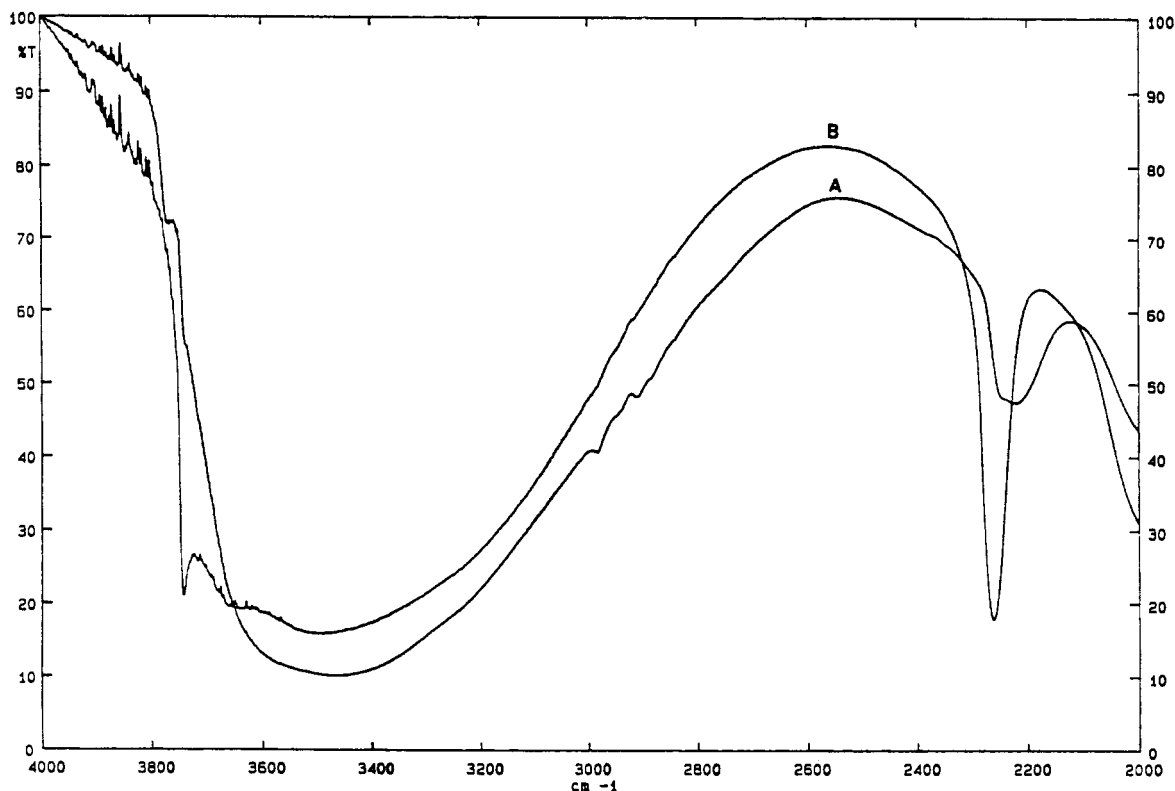


Figure 7. Partial (high-frequency range) DRIFT spectra of reduced silica before (A) and after (B) treatment with aqueous HCl.

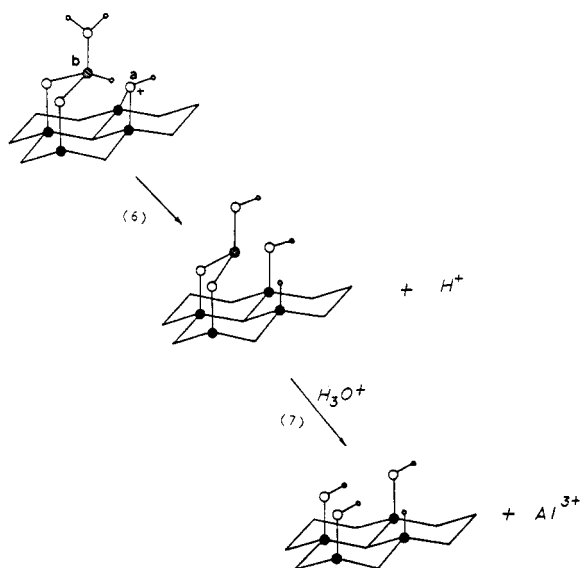


Figure 8. Reaction scheme for the acid treatment of reduced silica: (6) siloxane-bridge cleavage, (7) hydrolytic removal of chemisorbed aluminum; (filled circle) silicon, (open circle) oxygen, (dashed circle) aluminum, (small open circle) hydrogen.

silanols undergo rapid condensation, precluding a full development of the TGA peak.

Figure 12 illustrates typical DSC curves for reduced silica under inert (A) and oxidizing (B) atmospheres, respectively. Clearly, an exothermic peak at about 485 °C is a further confirmation of the occurrence of reaction 9. Subjecting the same oxidized sample to a second heating cycle showed no traces of an exothermic peak, indicating that a complete silane degradation had taken place during the first run. Unfortunately, the unavailability of appropriate standards precluded the use of DSC data for quantitative purposes.

Extent of Surface Reduction. As mentioned in the previous section, serious experimental complications prohibited the utilization of thermoanalytical data to determine the

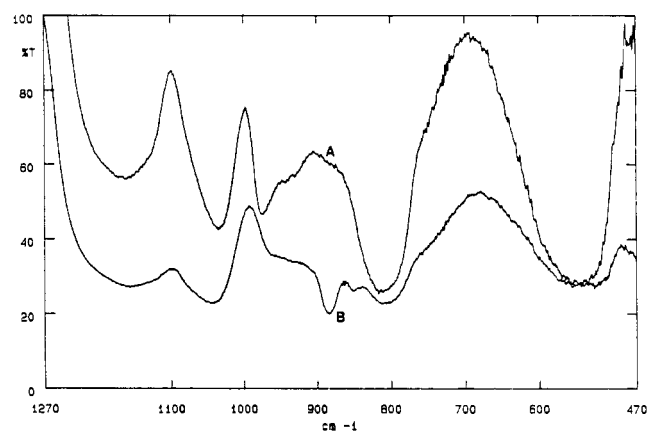


Figure 9. Partial DRIFT spectra of unreacted (A) and acid-treated reduced (B) silicas showing the absence and presence respectively of the SiH bending band. Curve A has been displaced upward for better illustration.

extent at which reduction of the silica surface has taken place. DRIFT information was used in a similarly qualitative fashion to monitor the SiH surface coverage by means of the characteristic (and strong) silane stretching band at 2260 cm^{-1} . Although this band was located in an interference-free IR region (Figure 7), its use for quantitative purposes was not possible because of experimental difficulties associated with lack of appropriate standards, a relatively low reproducibility in the preparation of the DRIFT sample surface, and a presumably poor linear dynamic range (12, 33), all leading to unreliable calibration.

In an alternate approach to determine silane surface coverage, the reducing ability of SiH species, in particular the reduction of certain metal cations such as Pd(II), Pt(II), Ag(I), and Hg(II), among others, was evaluated. It has been claimed (14) that reduction of the forementioned ions by poly(hydrosiloxane) xerogels occurred even in strongly acidic solutions and resulted in a metalized xerogel which no longer exhibited a hydrophobic behavior. When reduced silica was

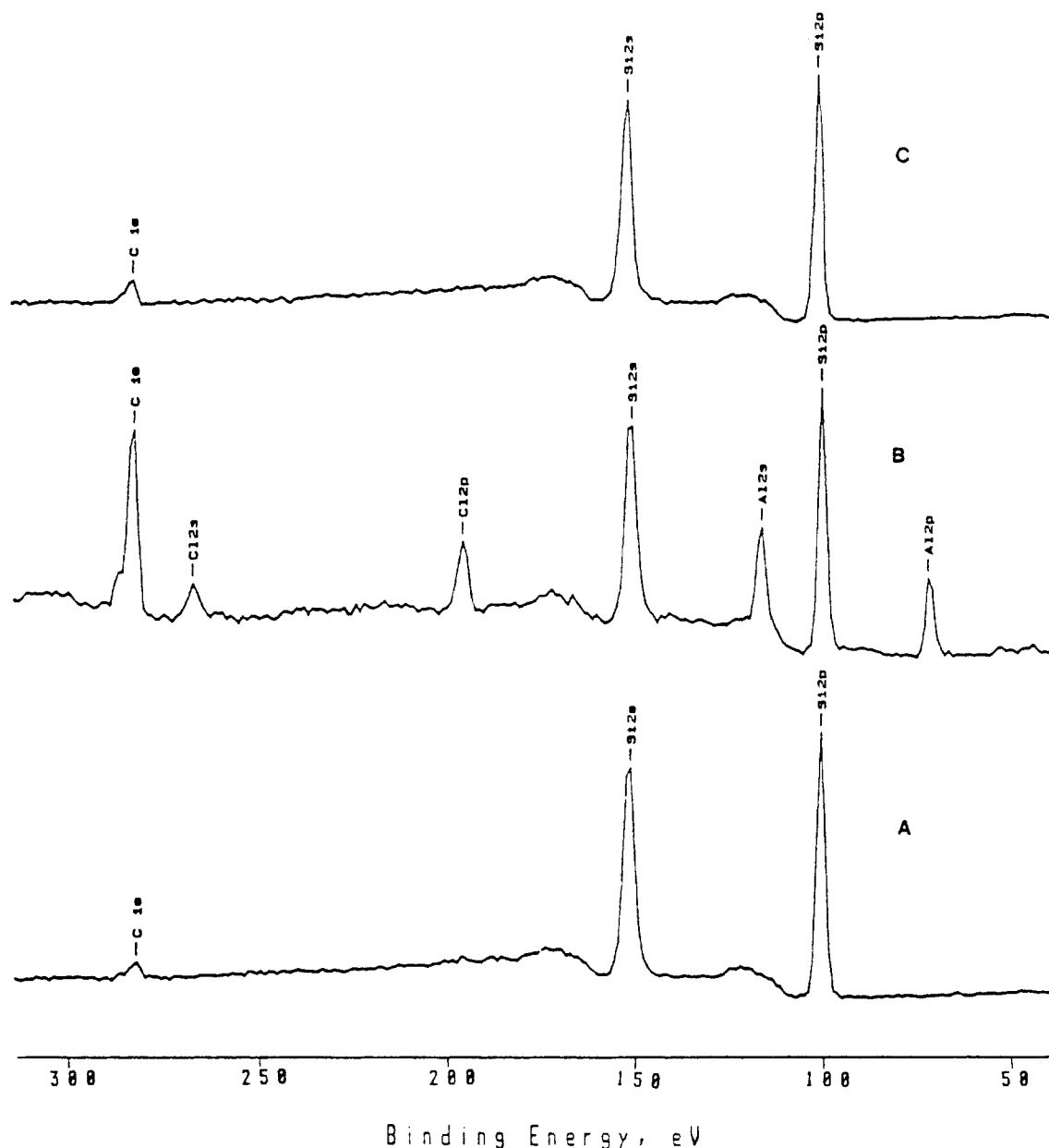


Figure 10. Partial ESCA spectra of silicas: (A) unreacted silica; (B) reduced silica (chlorinated A reacted with excess LiAlH_4) before HCl treatment; (C) product B after acid treatment.

treated overnight with an excess of 10 mM PdCl_2 solution in a 0.5 M HCl matrix, deep darkening of the solid support was readily observed. At the same time, extensive clearing of the supernatant liquid occurred along with a decrease in the concentration of the metal in solution (as confirmed by plasma emission spectrometry). However, testing the darkened solid by DRIFT showed that, even after a 48-h treatment period, the reduction did not proceed with complete consumption of silane as evidenced by the remaining of a strong SiH stretching peak. This is probably a result of the accumulative deposition of finely dispersed metallic particles which eventually clogged the pores and physically blocked further interaction of internal SiH species with metallic ions from the bulk liquid. No further attempts were made at this point to estimate the extent of surface SiH concentration.

CONCLUSIONS

The main goal of this part of the investigation was to produce a silica intermediate bearing surface silicon hydride species. This material was successfully produced by a chlorination/reduction procedure that sequentially converts the surface silanols into silicon chloride and then silicon hydride

groups. Final treatment of the reduced silica product with aqueous hydrochloric acid appeared to be an important synthetic step not only for an efficient removal of undesirable surface silane byproducts (as evidenced by ESCA data) but also as a means to further increase the formation of silane groups (as indicated by DRIFT evidence). Similarly with related materials from the literature (e.g. poly(hydridosiloxane) xerogels and certain H_2 -treated pyrolyzed silicas) the surface silane species were hydrolytically stable at low pH and thermally stable at temperatures up to 420 °C. Thermoanalytical information indicated that the surface silane species undergo complete oxidation when heated under an oxygen-containing atmosphere at temperatures above 470 °C.

We are presently developing methods for the surface hydrosilation of terminal olefins on the hydride-modified silica. While some parts of this subsequent work require carefully designed synthetic procedures and extensive spectroscopic characterization, preliminary experiments indicate that surface bonding does actually take place. This is evidenced, for instance, in the case of simple 1-olefins by the appearance of intense C-H stretching IR bands in the 3000–2800- cm^{-1} region concomitant with a considerable decline of the Si-H stretching

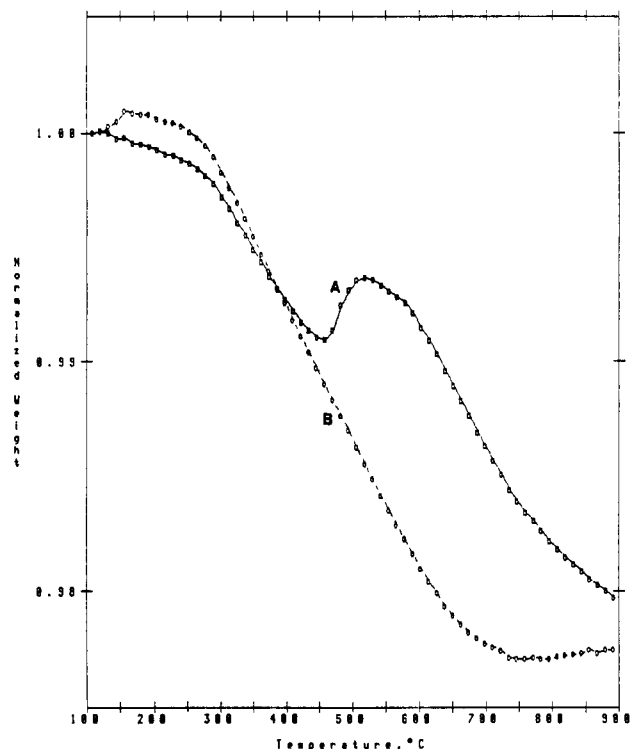


Figure 11. TGA curves of acid-treated reduced silica, in air (A) and N_2 (B).

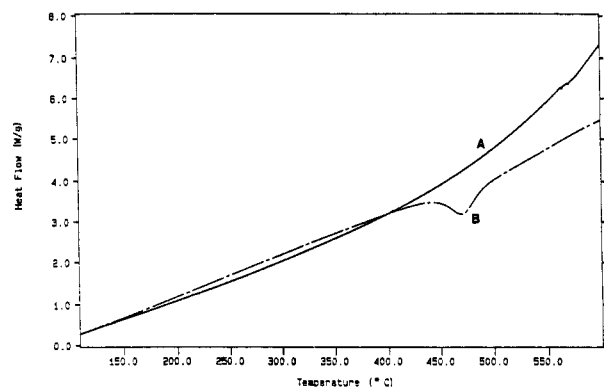


Figure 12. DSC curves of acid-treated reduced silica, in N_2 (A) and air (B).

band at 2260 cm^{-1} . Optimization of the extent of surface coverage as well as the application of this reaction to the attachment of a variety of vinyl-terminated organic moieties are currently under way. Additional research will also be undertaken in the evaluation of other substrates such as poly(hydridosiloxane) xerogels as alternate intermediates in the heterogeneous hydrosilation of terminal olefins.

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