Formation of New Materials with Thin Metal Layers through "Directed" Reduction of Ions at Surface-Immobilized Silyl Hydride Functional Groups. Silver on Silica

J. J. Reed-Mundell, Durgesh V. Nadkarni, Jerry M. Kunz, Jr.,
Christopher W. Fry, and James L. Fry*

Bowman-Oddy Laboratories, Department of Chemistry, The University of Toledo, Toledo, Ohio 43606-3390

Received March 13, 1995. Revised Manuscript Received June 23, 1995®

A novel two-step method is described for the controlled deposition of ultrathin layers of metals on surfaces originally having pendant hydroxy groups. The method is described here using silver on silica. "Reducing" silica was prepared easily by the reaction of trichlorosilane with silica gel. The product, characterized with ^{29}Si CP/MAS NMR and IR (DRIFT) techniques, displayed chemical reactivity expected of materials with covalently anchored SiH functional groups. This material was reactive toward aqueous and methanolic KF, methanolic HCl, and aqueous solutions of certain metal ions. Each SiH group was shown to function as an one-electron reducing site. Quantitative estimation of the surface-immobilized silyl hydrides was achieved using a gravimetric aqueous $AgNO_3$ method. Study by SEM X-ray dot mapping techniques of the material consisting of silver deposited by this manner on silica indicated uniform distribution of the silver across the surface, as defined by the original distribution of covalently attached SiH functions. In the presence of excess aqueous silver ions there was no increase in the total mass of silver deposited on the silica, but a slow redistribution of the silver into aggregates occurred. The silver was recovered quantitatively from the surface upon treatment with nitric acid.

Introduction

Many examples of surface-immobilized reagents applied to areas of industrial chemistry, chromatography, biochemistry, and preparative organic chemistry are known.[1] A reagent can be anchored onto a solid surface either by covalent bonding or through ionic interactions between the surface functional groups and the reagent.[1] We reasoned that if a reducing agent could be immobilized at well-defined sites on an existing surface, then it should be possible to reductively capture and immobilize metal ions dissolved in solution above the modified surface in a measured fashion. This ought to lead to an inherently new method for the controlled deposition of monatomic layers of metals on surfaces.

Hydride-donating reducing agents of boron, aluminum, and tin have been immobilized on solids such as silica gel and alumina. Although hydride-containing liquid silicon polymers are commercially available, silyl hydrides immobilized on solid surfaces are relatively unknown and rarely have been used for synthetic or other purposes.[2,3] On the basis of the known, rich chemistry of the SiH functional group, we predicted that materials with surface-immobilized silyl hydride groups would prove to have useful reducing properties.

A variety of organic and inorganic materials could be used for the immobilization or anchoring of silyl hydrides. Chemical modification is often easier with inorganic supports such as silica gel and alumina than with organic polymers. For this reason, we selected well-defined silica gel as the support for the initial preparation of immobilized silyl hydrides.[4]

We report here the preparation and characterization of surface-immobilized silyl hydrides on silica and a study of the material resulting from deposition of metallic silver on the "reducing silica" by reaction of aqueous silver ions with the SiH groups.

Experimental Section

General Techniques. All moisture-sensitive reactions were carried out under nitrogen or argon in oven-dried glassware. Dichloromethane (Aldrich), pyridine (Aldrich), and trichlorosilane (Aldrich) were distilled from calcium hydride under dry nitrogen. The silver nitrate (Fisher) was used without purification. Methanol was distilled from magnesium methoxide. All other reagents and solvents were purified according to published procedures.

Silica Gel. Both Merck Silica Gel G (BET surface area = 410–470 m^2/g) and Davisil chromatographic silica gel, 35–60 mesh, Grade 636, Type 60A (BET surface area = 485 m^2/g) were used as substrates for the silylation reactions. The silica gel was dried in a convection oven held at 140 °C for at least 60 h prior to use.

NMR. Solution nuclear magnetic resonance spectra were obtained on a Varian VXR-400 spectrometer instrument equipped with a ^{1}H–^{13}C switchable 5-mm probe. The spectra were run in $CDCl_3$ solvent without Me_4Si as an internal

---

® Abstract published in *Advance ACS Abstracts,* August 1, 1995.

[1] Laszlo, P., Ed. *Preparative Chemistry Using Supported Reagents*; Academic Press, Inc.: San Diego, 1987.

[2] (a) Sandoval, J. E.; Pesek, J. J. *Anal. Chem.* **1989**, *61*, 2067. (b) Sandoval, J. E.; Pesek, J. J. U.S. Patent 5,017,540, 1991.

[3] (a) Kini, A. D.; Nadkarni, D. V.; Fry, J. L. *Tetrahedron Lett.* **1994**, *35*, 1507. (b) Fry, J. L.; Nadkarni, D. V. U.S. Patent 5,281,440, 1994.

[4] Ford, W. T.; Blossey, E. C. In ref 1, Chapter 12.

0897-4756/95/2807-1655$09.00/0

standard. All ^{29}Si cross-polarization/magic-angle-spinning nuclear magnetic resonance spectra were obtained on a Chemagnetics CMC-200 (solids) NMR spectrometer operating at 39.73 MHz with Me_4Si as an internal standard. The sweep width used was 20 kHz, contact time 5 ms, acquisition time 0.20 s, and spinning rate 5 kHz.

IR. Infrared spectra were run on either Nicolet 60 SX or 5 DX FTIR spectrophotometers. Infrared spectra of silica gel-immobilized silyl hydrides were taken on a Nicolet 60 SX FTIR spectrometer using the diffuse reflectance infrared Fourier transformation (DRIFT) technique.[5]

SEM. All secondary electron, X-ray energy-dispersive analysis, and dot mapping were obtained with a JEOL JSM-6100 SEM equipped with CLD20 and CLD201 detectors and a thermal emission type electron gun employing a LaB_6 cathode. An Analytical Link eXL was used for acquisition and storage of X-ray spectra.

Treatment of Silica Gel with Trichlorosilane. *Method Using Pyridine.* Dried silica gel (40 g) was transferred into a three-necked 3000-mL flask equipped with a water condenser, mechanical stirrer, and an addition funnel. Freshly distilled trichlorosilane (Aldrich, 125 mL, 1.24 mol) in 800 mL of dry CH_2Cl_2 was added to the silica gel under an argon atmosphere. The reaction mixture was cooled to −78 °C with dry ice and acetone. Pyridine (300 mL, 3.71 mol) was added slowly dropwise from an addition funnel to the reaction mixture at −78 °C with intermittent stirring. A thick precipitate of pyridinium chloride formed in the reaction flask. An additional 400-mL portion of dry CH_2Cl_2 was added to the reaction mixture, and the mixture was stirred at room temperature under argon for 24 h. The reaction mixture was then again cooled to −78 °C, and dry methanol (400 mL) was added slowly to the mixture dropwise. The reaction mixture was filtered on a Buchner funnel, and the silica gel was washed further with 1000 mL of dry methanol to dissolve and remove the pyridinium chloride precipitate. Finally, the silica gel was washed with CH_2Cl_2 (500 mL). This modified silica gel product was then dried at 110 °C for 8 h under aspirator vacuum. The IR (DRIFT) spectrum showed absorptions at 2253, 2852, 2952, and 3563 cm^{-1}; ^{29}Si NMR (CP/MAS) δ −74.6 (SiH), −85.0 (SiH), −101.7, and −111.1 ppm. Silver ion analysis showed 2.0 mmol of SiH/g of silica gel.

Method without Pyridine. Dried silica gel G (50 g, BET surface area = 410−470 m^2/g) was transferred into a three-necked 1000-mL flask equipped with an addition funnel and a Dewar condenser filled with crushed dry ice in isopropyl alcohol and vented through a Drierite-filled drying tube. The silica gel was slurried by the addition of 150 mL of dry CH_2Cl_2. Freshly distilled trichlorosilane (Aldrich, 15.2 mL, 0.151 mol) was added dropwise through the addition funnel, with hand swirling, to the CH_2Cl_2 slurry of silica gel over a period of ca. 30 min. It was then cooled to 0 °C with an ice bath, and 50 mL of anhydrous methanol was slowly added dropwise from the addition funnel with intermittent stirring over a period of 0.5 h. The reaction mixture was filtered on a Buchner funnel and the silica gel was washed five times with 50 mL portions of dry methanol. This modified silica gel product was then dried at 110 °C for 8 h under aspirator vacuum. The IR (DRIFT) spectrum was essentially the same as that of the product prepared by the method using pyridine. Silver ion analysis showed 2.4 mmols of SiH/g of silica gel.

General Procedure for the Quantitative Estimation of Silyl Hydrides on the Surfaces of Silica Gel. The following procedure for the estimation of silyl hydrides on the surface of silica gel is representative. Silver nitrate crystals were crushed and the powder was dried in an oven at 140 °C for 2 h. Dry silver nitrate (3.75 mmol, 0.6370 g) was dissolved in 50 mL of distilled water in a volumetric flask. Silica gel-immobilized silyl hydride (1.000 g) was placed in a 250-mL round-bottomed flask. The silver nitrate solution made as above was added to this silica gel. The volumetric flask was rinsed with 20 mL of distilled water, and the washings were added to the silica gel. An immediate black precipitation was observed after the addition of silver nitrate solution to the silica gel-immobilized silyl hydride. The solution was covered to exclude light and stirred with a magnetic stirrer for 24 h, and the solution was then filtered through a Buchner funnel. The silica gel was washed with 50 mL of distilled water to remove traces of unchanged silver nitrate. The DRIFT spectrum of the silica gel following this treatment was devoid of any bands related to the SiH group. To the filtrate was added 5 drops of 1% HNO_3 solution. The solution was then warmed to 50−60 °C. Silver chloride was precipitated out by adding 0.2 M aqueous HCl solution dropwise to the filtrate (unchanged silver nitrate solution). During the precipitation, the temperature was kept at around 50−60 °C. The precipitate was allowed to settle in the flask in a dark place for 2 h at room temperature. The supernatant liquid was tested for further precipitation with aqueous HCl solution. The precipitate was allowed to settle in the flask in a dark place overnight (12−16 h). The silver chloride precipitate was then filtered through a preweighed Gooch sintered crucible (30 mL, Pyrex, F) under aspirator vacuum, and the precipitate was washed with 20−25 mL of dilute HNO_3 solution (0.2 mL of concentrated HNO_3 diluted to 200 mL with distilled water). This was followed by washing with 100 mL of distilled water. The precipitate was dried in an oven at 140 °C for 24 h and then weighed.

The following relationships were used to calculate the concentration of active surface-immobilized SiH functions on the sample:

$$\text{moles of silver chloride} = \text{moles of unchanged silver nitrate}$$

$$\text{moles of original silver nitrate} - \text{moles of unchanged silver nitrate} = \text{moles of silver nitrate consumed}$$

$$\text{moles of silver nitrate consumed} = \text{moles of SiH present}$$

Establishment of Stoichiometry of Silver Ion Reduction by Trimethoxysilane. A solution containing 0.6379 g (3.75 mmol) of silver nitrate in 50 mL of water was stirred with 0.127 mL (0.122 g = 1.00 mmol) of trimethoxysilane. Immediately a dark precipitate formed. Following 24 h of stirring, the precipitated colloidal silver metal was filtered off in a Buchner funnel. The supernatant was treated with 0.2 M HCl to cause precipitation of remaining silver ion as AgCl. After filtration onto a Buchner funnel, washing, and drying, there was obtained 0.3920 g (2.735 mmol) of AgCl precipitate. Thus, 1.02 mmol of Ag^+ reacted with 1.00 mmol of trimethoxysilane.

General Procedure for the Quantitative Estimation of Silver Metal Deposited on the Surface of the Derivatized Silica Gel. The following procedure for the estimation of silver metal deposited on the derivatized silica gel is representative. A 0.1332 g sample of silver-metalated silica gel was treated with 1.5 mL of concentrated nitric acid and diluted with 20 mL of distilled water. The original black color of the sample immediately discharged resulting in a white residue. The mixture was filtered through a Hirsch funnel under an aspirator through 595 filter paper (Schleicher and Shuell). The clear colorless filtrate was treated with 20 mL of saturated NaCl solution. The white precipitate was filtered as above. After the residue was rinsed with distilled water, the sample was dried under vacuum at 100 °C for 3 h. There was obtained 0.0324 g of silver chloride. Thus, the original metallic silver loading was equal to 2.1 mmol of SiH/g of silica gel.

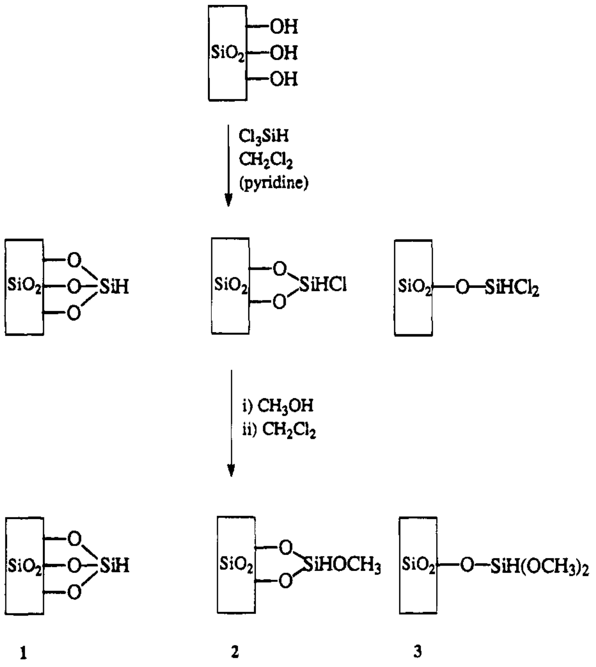
Results and Discussion

Modification of Silica Gel. The chemistry used for direct silane coupling reactions to inorganic polymer supports having pendant hydroxy groups has been well

---

(5) Davies, J. A.; Sood, A. *Makromol. Chem.* **1985**, *186*, 1631.

Scheme 1

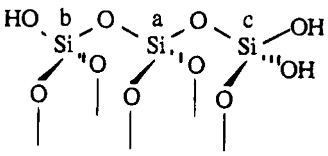


worked out. Procedures for the reaction of silica gel with silanes of the type X_3Si-R have been described.[6] It is known that the reactions of silica gel with alkyltrichlorosilanes are more facile than those with alkyltrialkoxysilanes.[7] For reasons of economy and simplicity, we decided to treat silica directly with trichlorosilane.

For our experiments we selected commercially available high surface area silica gel for the reaction with trichlorosilane. The dried silica gel was treated with trichlorosilane in methylene chloride either with pyridine to remove the hydrogen chloride formed or without the pyridine and then washed with dry methanol and methylene chloride prior to drying (Scheme 1). Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT)[5] and ^{29}Si cross-polarization/magic-angle-spinning (CP/MAS) nuclear magnetic resonance techniques were found to be satisfactory for identifying the nature of the SiH functional group on the surface of the resulting product.[8]

The DRIFT spectrum of the trichlorosilane-modified silica gel showed a strong Si–H stretching vibration at 2253 cm^{-1}, which is characteristic of the SiH group when bonded as $(RO)_3SiH$.[9] A broad absorption centered in the hydroxy region (3563 cm^{-1}) indicated the presence of unchanged hydroxy groups. This is clearly related to the inaccessibility of some hydroxy groups to trichlorosilane. Two intense bands at 2952 and 2852 cm^{-1} were assigned to C–H stretching vibrations. This indicated the presence of some $-OCH_3$ groups on the surface of the silica gel.[5] These C–H stretches were not due to residual methanol adsorbed on the silica gel. This was confirmed by a control experiment in which dry silica gel was stirred with methanol, filtered, and dried at 110 °C for 8 h in a drying pistol. The DRIFT spectrum of this silica gel showed no C–H stretching bands.

The ^{29}Si solid-state CP/MAS NMR spectrum of the original dry, untreated silica gel showed the expected three peaks arising from three different types of Si atoms (a–c) present in the silica gel (**4**).[10]



4

The ^{29}Si CP/MAS NMR spectrum of the trichlorosilane-modified silica gel showed the presence of two new signals at δ −75 and −85 ppm in addition to the signals from the silicon atoms already present in the backbone of silica gel. The signal related to silicon atom c had disappeared after treatment, and the intensity of the signal related to silicon atom b was sharply reduced. This is indicative of the reaction of the trichlorosilane with the pendant hydroxy groups present on the silica gel.[11]

As shown in Scheme 1, there can be three modes of attachment of trichlorosilane to the surface of the silica gel, potentially giving rise to species **1**–**3**. The two new peaks at δ −75 and −85 ppm in the ^{29}Si NMR spectrum belong to Si atoms bearing hydrogen.[11] The combined spectroscopic data thus unambiguously show the presence of both SiH and $Si(OCH_3)H$ groups on the surface of the silica gel that was treated first with trichlorosilane and then with methanol.

Reactions of Si–H Modified Silica Gel. *Solvolysis.* The reaction of trichlorosilane-modified silica gel with aqueous KF resulted in complete removal of Si–H from the surface as evidenced by the disappearance of the Si–H stretch in the DRIFT spectrum of the resulting silica gel. This is as expected for fluoride-catalyzed hydrolysis of the SiH functions back to SiOH groups.[12] To investigate the reactivity of the surface hydrides toward strong electrophiles such as HCl, the trichlorosilane-modified silica gel was treated with methanolic HCl and the reaction mixture was stirred for 24 h. After a methanol wash, the silica gel was dried at 110 °C for 10 h. In contrast to the vigorous reaction that occurred with aqueous KF, the reaction with HCl was found to be sluggish. The infrared spectrum (DRIFT) of this silica gel showed the presence of a weak, residual Si–H stretch.

Metalation of Substrate Surface. Since silver ions (Ag^+) are readily reduced by silyl hydrides,[13] deposition of elemental silver onto the silica surface is achieved by reacting an aqueous silver nitrate solution with the immobilized silyl hydride (eq 1). This self-limiting

---

(6) Waddell, T. G.; Leyden; D. E.; Hercules, D. M. In *Silylated Surfaces*; Leyden, D. E., Collins, W. T., Eds.; Gordon and Breach: Science Publishers: New York, 1980; p 55.

(7) Murrell, L. L. In *Advanced Materials in Catalysis*; Burton, J. L., Garten, R. L., Eds.; Academic Press: New York, 1977; Chapter 8.

(8) Spectra available as supporting information.

(9) Smith, A. L.; Angelotti, N. C. *Spectrochim. Acta* **1959**, *15*, 412.

(10) (a) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 4263. (b) Sindorf, D. W.; Maciel, G. E. *J. Phys. Chem.* **1982**, *86*, 5208.

(11) Rudzinski, W. E.; Montgomery, T. L.; Frye, J. S.; Hawkins, B. L.; Maciel, G. E. *J. Catal.* **1986**, *98*, 444.

(12) Semiquantitative volumetric analysis of the flammable gas evolved over the KF-catalyzed hydrolysis was in agreement with the gravimetric determination of the amount of SiH groups immobilized on the surface of the silica gel when the stoichiometry of eq 1 was applied. The hydrolysis of the SiH functions follows the equation: $\equiv SiH + H_2O \rightarrow \equiv SiOH + H_2$.

(13) Anderson, H. H. *J. Am. Chem. Soc.* **1958**, *80*, 5083.

$$\boxed{SiO_2}\text{—OSiH} + Ag^+ + 2H_2O \longrightarrow \boxed{SiO_2}\text{—OSiOH} + Ag^0 + H_3O^+ + 1/2H_2 \qquad (1)$$

procedure not only yields an ultrathin silver surface on the silica but also provides a quantitative method for determining the concentration of immobilized silyl hydrides.

(a) Quantitative Estimation of SiH on the Surface. For any surface-immobilized reagent to be synthetically useful, it is essential to know the amount of the active species or functional groups present on the surface of the supporting material. In cases where the functional groups are carbon or heteroatom based, the determination can be achieved by quantitative elemental analysis. However, in the present system where silyl hydrides were immobilized on the surface, the small atomic weight of hydrogen does not make any significant contribution to the total weight of the material.[12] Several analytical methods have been reported in the literature for the quantitative estimation of SiH functions in solution.[14] Unfortunately, the two principal methods normally used, namely, those involving the reaction of SiH groups either with Br_2[15] or with mercuric chloride,[16] did not seem appropriate for the heterogeneous case at hand. On the other hand, the reduction of aqueous silver ions seems not to have been used previously for the quantitative determination of silyl hydrides. We have now applied this reaction to estimate the concentration of the surface-immobilized silyl hydride functions on the silica gel.

This method of estimation of silyl hydrides on the solid surfaces was repeated several times and with different batches of material that had been modified with trichlorosilane either using or omitting pyridine in the preparation (see Experimental Section). The method was found to be highly reproducible. Repeated analyses of material obtained by using the same amount of silica gel and trichlorosilane consistently yielded 2.0 mmol of SiH/g of silica gel product when pyridine was used and 2.1−2.4 mmol of SiH/g of silica gel product when pyridine was omitted in the preparation. The fact that silver was not retained on the surface of the unmodified silica gel was determined by treatment of regular silica gel with aqueous silver nitrate solution under conditions identical to those used for the previous estimations. In these experiments the silver ions were quantitatively recovered from the solution as AgCl precipitate. The stoichiometry of the reduction of silver ions by Si−H was confirmed by the reaction of a known amount of trimethoxysilane with a known excess of aqueous silver nitrate solution. The excess of silver ions was then determined gravimetrically as described above. It was found that 1 equiv of silver nitrate was needed to oxidize 1 equiv of trimethoxysilane. This confirmed the one-electron nature of this reduction reaction.

(b) Characterization of Metalated Surface. Two major challenges faced in thin-layer metal deposition are control of the degree of dispersion of the metal on the substrate surface and the amount of metal loaded per gram of substrate. For example, fabrication of microelectrodes and other microcircuitry needs require a well-controlled metal deposition process. We discovered in this work that prolonged contact of the silver nitrate solution with the previously derivatized silica surface caused a progressive increase in the size of silver clusters on the surface. By running a series of timed depositions from 0.5 to 72 h, we observed a substantial change in the dispersion of the deposited silver.

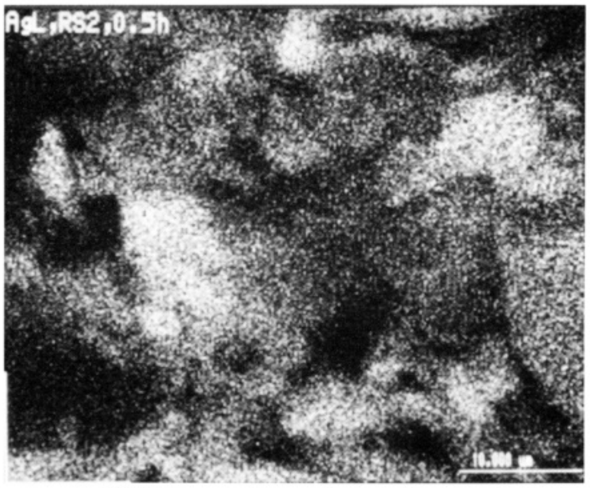


Figure 1. SEM X-ray dot mapping of silver on derivatized silica surface after 30-min treatment with excess aqueous silver nitrate. Lower right-hand scalar bar represents 10.00 μm.

Elemental dot mapping and X-ray dispersive analysis indicated the formation of a highly dispersed layer of metallic silver onto the derivatized silica gel after a 30-min treatment with aqueous excess silver nitrate solution (Figure 1). This process created microcrystals of metallic silver with dimensions less than 1 μm.

The amount of metal loading at the silica surface was determined by first treating the metalated silica with concentrated nitric acid. This caused the deposited silver to be oxidatively removed from the surface. The amount of dissolved silver ions was then gravimetrically determined by subsequent treatment of the solution with excess chloride ion. Results indicated an initial metal loading of 0.8 mmol of Ag/g of silica. It was further demonstrated that extended exposure of the treated silica with aqueous silver nitrate increased the metal loading up to, but not exceeding, 2.1−2.4 mmol of silver/g of silica (i.e., the maximum concentration of surface silyl hydrides). Samples that were allowed to remain in contact with the aqueous silver nitrate for longer periods of time also indicated progressive increase of silver clustering. It is of interest that with increased clustering the mass of silver on the silica surface remained constant.

SEM dot mapping indicated that after 5 h (Figure 2a) of exposure to excess aqueous silver nitrate, silver clusters with sizes up to approximately 1 μm in dimension were observed at the surface. After 20 h (Figure 2b) the numbers of the clusters increased although the individual dimensions remained approximately the same. A 72 h exposure to aqueous silver nitrate yielded surface clusters of silver measuring greater than 10 μm (Figure 2c).

This progressive clustering also was demonstrated with samples that had been initially treated 30 min with

---

[14] Crompton, T. R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley and Sons: Chichester, 1989; Chapter 6.

[15] Fritz, G.; Burdt, H. *Anorg. Chem.* **1962**, *317*, 35; *Chem. Abstr.* **1962**, *57*, 14437g.

[16] Kreshkov, A. P.; Bork, V. A.; Shvyrkova, L. A. *Zh. Anal. Khim.* **1962**, *28*, 151; *Chem. Abstr.* **1962**, *57* 1550c.

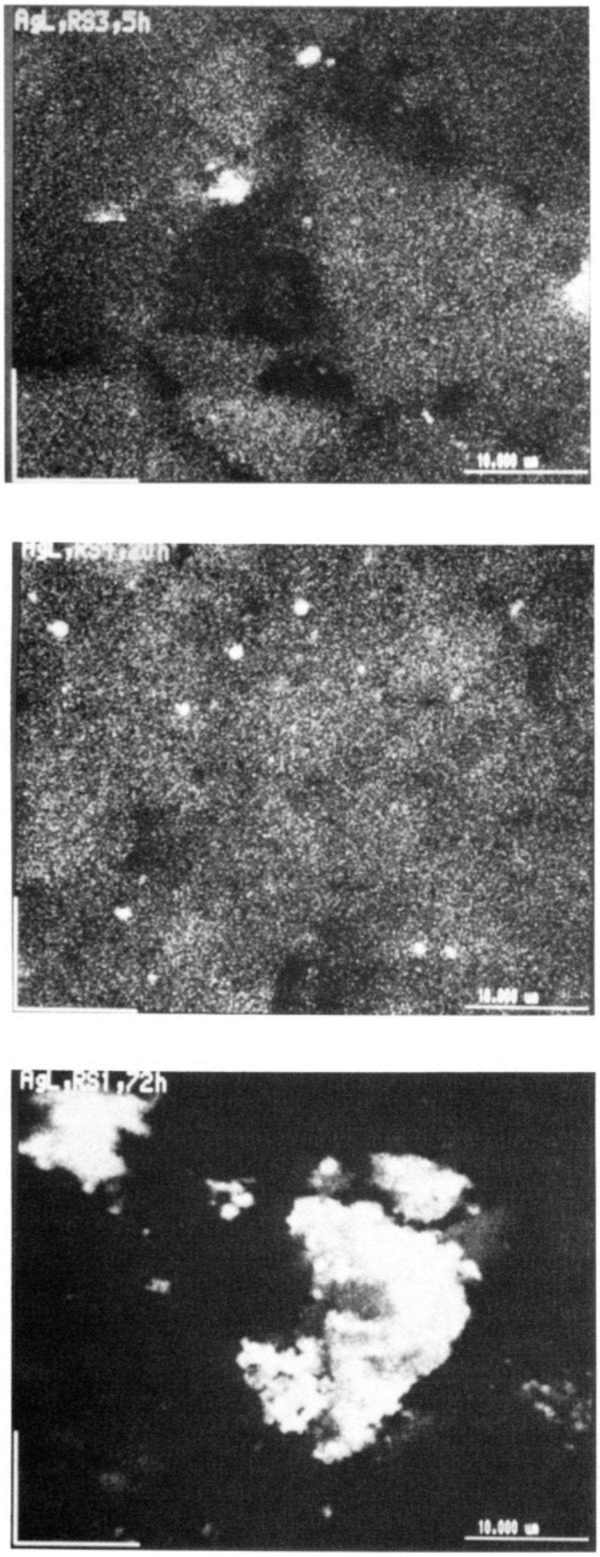


Figure 2. SEM X-ray dot mapping of silver on derivatized silica surface after: (a, top) 5 h, (b, middle) 20 h, and (c, bottom) 72 h treatment with aqueous excess silver nitrate. Lower right-hand scalar bar represents 10.00 μm.

aqueous silver nitrate, isolated from solution, and then at a later time again treated with aqueous silver nitrate. Similar samples (i.e., 30 min Ag deposition time) further treated with aqueous sodium nitrate instead of aqueous silver nitrate did *not* exhibit any further change in the initial metal dispersion, thus establishing the necessary presence of excess silver ions in order for silver metal redistribution to occur.

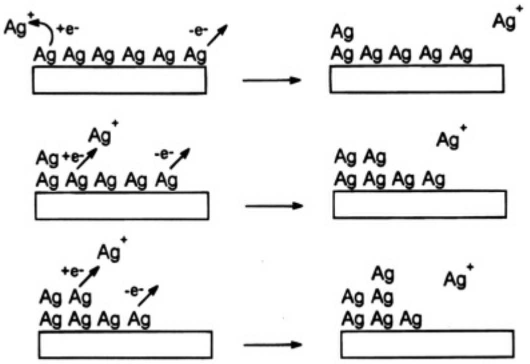


Figure 3. Schematic representation of a mechanism for the redistribution of primary mode deposited silver on a silica surface by the one-electron redox action of excess Ag^+.

The observation of the time-dependent metal clustering along with a metal loading which does not exceed the surface concentration of hydrosilanes led us to hypothesize two mechanisms of metal deposition. The first mechanism (eq 1), as previously discussed, involves the primary site-specific reduction of aqueous Ag^+ ion with concomitant deposition of elemental silver. A second mechanism (Figure 3) may now be considered in which an equilibrium of the Ag/Ag^+ couple is established between surface-immobilized elemental silver and the soluble silver ions. This redistribution process can occur either in close proximity or at long range, involving a constant exchange of silver atoms at the surface through oxidation–dissolution of the originally deposited surface metallic species and reduction–deposition of the mobile ionic species.

This process of secondary deposition may take place at unoccupied sites or at thermodynamically favored metalated positions, where these latter positions can act as seeding centers for the agglomeration of silver. As the metal loading reaches its limit, the secondary deposition would occur more frequently at metalated sites, thus increasing the rate of clustering. This process is undoubtedly driven by reduction in the net free energy of the system as the silver metal redistributes itself into microcrystals.

Conclusion

In summary, we have presented a novel, effective technique for the site-directed reductive deposition of elemental silver onto derivatized silica gel. Through SEM analysis we have determined time-dependent depositions ranging from a highly dispersed metalated surface with a metal loading of 0.8 mmol of Ag/g of silica to silver cluster formation with sizes greater than 10 μm at a maximum metal loading of 2.1–2.4 mmol of Ag/g of silica.

We also reported the characterization and quantitative estimation of silyl hydride functional groups immobilized on solid silica gel support. A chemical method employing aqueous silver nitrate was devised for the quantitative estimation of the surface-immobilized silyl hydrides.

It is important to emphasize that this immobilization technique should be broadly applicable to permit the covalent attachment of SiH functions to a wide variety of materials having pendant surface hydroxy groups. Both naturally occurring and synthetic materials should be amenable to this treatment, from polyols to saccharides to metal oxides. The resulting derived metal-deposited materials in many cases would be expected to possess novel properties useful for applications in such areas as microelectronics and catalysis.[17]

Acknowledgment. We thank Dr. Gregory A. Nemeth for running ^{29}Si CP/MAS NMR spectra for the characterization of the surface-immobilized silyl hydrides. We are grateful to Professors James E. Gano and Julian A. Davies for their comments and suggestions during the course of this study, to Ms. Pannee Burckel for SEM analysis, and to Mr. Abhay Kini and Mr. C. W. Gundlach for their help with experimental procedures. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to The University of Toledo Faculty Research Awards and Fellowship Program for support of this work.

Supporting Information Available: DRIFT and CP/MAS ^{29}Si NMR spectra of silica gel before and after treatment with Cl_3SiH and CH_3OH (2 pages). Ordering information is given on any current masthead page.

CM950110I

---

(17) Nadkarni, D. V.; Fry, J. L. *J. Chem. Soc., Chem. Commun.* **1993**, 997.