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Role of surface-adsorbed water in the horizontal polymerization of trichlorosilanes

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Abstract

The high surface area of porous silica gel enables characterization of the amount of adsorbed water needed for horizontal polymerization of trichlorosilanes for the first time. Silica gel samples were individually exposed to relative humidity levels of 30%, 40%, 50% and 60% prior to reaction, and the amount of adsorbed water was determined by weighing. Optical microscopy shows that polymer microspheres, unattached to the silica, form in the case of 60% humidity, indicating that this level is in excess of the optimum coverage of water. Microanalysis reveals a monotonic increase in carbon with increased humidity, and ^{29}Si NMR spectra reveal increased cross-linking of the siloxanes as the humidity increased to 50%. HPLC is shown to be a very sensitive technique for assessing the coverage of the silica substrate: zone tailing is sharply minimized at 50% humidity. These results point to 50% as the optimal humidity for dense horizontal polymerization of trichlorosilanes. The amount of adsorbed water at 50% humidity and room temperature is $22 \pm 3 \mu\text{mol}/\text{m}^2$, which approaches the stoichiometric amount required to hydrolyze the trichlorosilanes. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

The silica substrate is well known to cause tailing of organic bases in liquid chromatography due to acidic sites on the surface [1–3], which adsorb strongly at low concentrations of analyte [4]. The silica substrate also limits the pH range of liquid chromatography because strong base attacks silica, leading to dissolution of the stationary phase [5,6]. Providing a barrier between the silica and the mobile phase can reduce these two problems. Endcapping is widely used to provide such a barrier, giving a reduction in tailing of organic bases and an increase

in hydrolytic stability at high pH [7]. Horizontal polymerization of trichlorosilanes has been introduced as a different means of placing a barrier between the silica substrate and the mobile phase [8]. In this case, the barrier is created by dense two-dimensional cross-linking of reagent groups so that oriented methyl spacers protect the silica. These stationary phases also exhibit high stability and low silanol activity [9,10].

One difficulty in reproducing horizontally polymerized stationary phases is the need for humidification of the silica substrate, which provides reagent water for hydrolysis of the trichlorosilanes. Different silica samples require different levels of humidity [10], presumably due to their different adsorptivities

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of water. There has been considerable discussion and awareness of the need for some amount of water for self-assembly of trichlorosilanes, based on studies with flat surfaces [11–16]. However, none of these studies prescribes the amount of adsorbed water because of the lack of tools applicable to low surface areas. It has been suggested from studies of multilayers of trichlorosilanes on flat surfaces that a stoichiometric amount of water is required [17], however, this idea has not been tested experimentally for monolayers. It is crucial to determine the optimal amount of adsorbed water for chromatographic use because of the exceptionally high requirements for performance and reproducibility in chromatography.

The purpose of this work is to investigate the amount of water needed to synthesize a densely cross-linked horizontally polymerized trifunctional silane monolayer on fully hydroxylated silica gel. The high surface area of chromatographic silica gel uniquely affords the ability to quantify the amount of adsorbed water by direct weighing of the silica gel. Carbon microanalysis determines whether or not the amount of carbon per area agrees with high monolayer density. ^{29}Si NMR spectroscopy probes the extent of reagent cross-linking after reaction. Chromatographic elution at pH 8 of the doubly charged cationic probe, tris(2,2'-bipyridyl)ruthenium II, senses exposed substrate through electrostatic interactions [18].

2. Experimental section

2.1. Materials

n-Octadecyltrichlorosilane and methyltrichlorosilane were purchased from United Chemical Technology (Piscataway, NJ, USA) and were used within weeks of being received. Tris(2,2'-bipyridine)ruthenium chloride ($\text{Ru}(\text{bpy})_3^{2+}$) was purchased from Aldrich (Milwaukee, WI, USA). The heptane was purchased from Aldrich and was subsequently filtered through a dried silica and aluminum oxide column to remove any water or other polar impurities. Deionized water was further purified to a resistance of 18 MW-cm using a Barnstead E-Pure system.

2.2. Synthesis of the stationary phases

Kromasil silica (5.6 μm diameter, 100 \AA pore size, 350 m^2/g surface area) was used in these experiments. The procedure for the mixed horizontal polymerization was described previously [9]. Silica samples of 5 g were cleaned in a boiling mixture of nitric acid and water (50:50, v/v), and then rinsed with an abundant amount of water until the pH of the filtrate was neutral. The silica was then dried at 100°C under a continuous N_2 blanket using a Sybron Thermolyne Type 21100 tube furnace. Water was adsorbed to the dried silica by flowing humidified nitrogen through the silica until the humidity at the outlet equalled the humidity at the inlet for at least 1 h. This procedure required many hours for each silica sample. Shorter equilibration times were found to give poor reproducibility. Silica samples were exposed to relative humidity levels of 30%, 40%, 50% and 60%, with three replicates for each humidity level. The water coverage at each humidity level was determined by sealing off the humidification chamber and weighing it. The average for the three replicates is reported.

After humidification and weighing, the silica was placed in a reaction vessel under a blanket of nitrogen, along with a stirring bar and 20 ml of filtered heptane. A reagent ratio of 6:1, *n*-octadecyltrichlorosilane to methyltrichlorosilane, at a 1.2 times molar excess, was used to achieve the 1:3 ratio of $\text{C}_{18}:\text{C}_1$, as described previously [9,19]. The reagents were added slowly from a syringe over a period of 1 min to the stirring silica. After addition of the reagent, the flow of nitrogen was continued to purge the evolving HCl gas. The flask was then capped and the reaction was allowed to proceed for 18 h. The derivatized silica was then rinsed with 200 ml each of fresh heptane, methylene chloride, and methanol, and dried for 2 h at 120°C. The carbon content for each of the silica samples was evaluated by Microanalysis, (Wilmington, DE, USA).

2.3. NMR measurements

The NMR spectroscopy has been described previously [19]. The ^{29}Si NMR experiments were performed with a Bruker MSL 300 Fourier Transform

instrument, which employed a 90° pulse width of 6 ms at 59.6 MHz. All experiments used cross-polarization to enhance the signal-to-noise ratio. The contact time was 5 ms and the relaxation delay was 5 s for the 5000 scans. A sample of 2,2 dimethyl-2 silapentane-5 sulfonic acid was used to achieve the Hartmann–Hann match, and magic angle spinning at 3.0 kHz was used. Absolute intensity mode was used to compare the data. A 15-h data acquisition time was used for each sample, and 10 Hz line broadening was introduced to enhance signal-to-noise ratio.

2.4. Chromatography

The stationary phases used in these experiments were packed into 7.5 cm×0.46 cm columns, using a Haskel pump and a silica slurry of 50:50 cyclohexanol and methylene chloride. Acetonitrile was used as the packing liquid at a pressure of 5200 psi. A 60:40 (v,v) mobile phase of acetonitrile and water was used in these experiments, and was prepared as follows. The 18 M Ω -cm water was degassed with helium, and its pH was adjusted to 8 by titration with NaOH. The requisite amount of NaCl was added to bring the ionic strength up to 0.01, and the resulting aqueous solution was mixed with acetonitrile to give the 60:40 ratio of volumes.

A Hewlett Packard 1090 HPLC was used for all chromatographic measurements. A flow of 1 ml/min and a detector response time of 1 ms were used. The detector wavelength was 268 nm, the oven temperature was 30°C and the injection volume was 10 μ l. Concentrations of 60, 100, 140, and 200 mM Ru(bpy)₃²⁺ were used, and four injections at each concentration were made for each column.

3. Results and discussion

Fig. 1 shows a plot of equilibrium water coverage vs. relative humidity for four replicate silica samples at each of the four humidity levels. The coverages from 30% to 60% humidity represent a range of 7±3 to 35±2 μ mol/m² of adsorbed water. A monolayer of water is expected to have a coverage of 15 or 17 μ mol/m², depending on whether the adsorbed layer has a water or an ice density, respectively. The solid

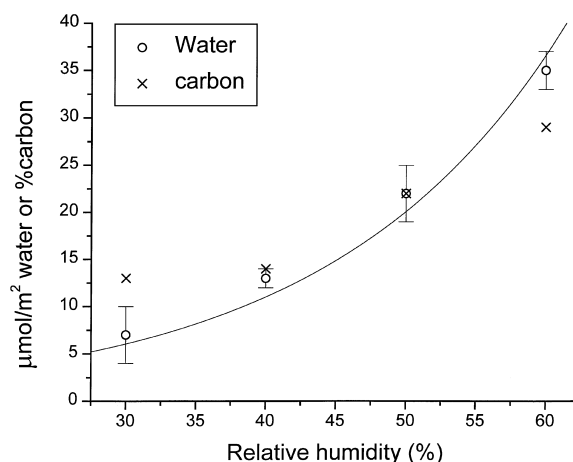


Fig. 1. Plot of the coverage of water and the percentage of carbon vs. relative humidity at room temperature for Kromasil silica gel.

line in Fig. 1 shows that a nonlinear relation describes the data, with the water coverage growing exponentially.

$$w = \exp(0.06 \cdot \%H) \quad (1)$$

The exponential growth indicates that the increasing amount of adsorbed water progressively makes the surface more attractive for further adsorption of water.

After reaction with the trichlorosilanes, the samples were examined by optical microscopy. For the samples made at 30, 40 and 50% humidity, only the expected particles of 5 μ m in diameter were observed. For the sample made at 60% humidity, numerous particles of approximately 1 μ m in diameter were observed, as shown in Fig. 2. This reproducible effect is attributed to the polymerization of excess reagent beyond that which can covalently attach to the surface.

The amount of carbon detected by microanalysis was found to increase with humidity, although not in proportion to humidity. The carbon percentage is included in Fig. 1. Table 1 lists both the initial water coverage and final carbon coverage at each humidity level. At 30% humidity, the amount of carbon is disproportionately high relative to the water coverage. This is likely due to the fact that the trichlorosilanes can react with surface silanols directly. At 60% humidity, the amount of carbon is dispropor-

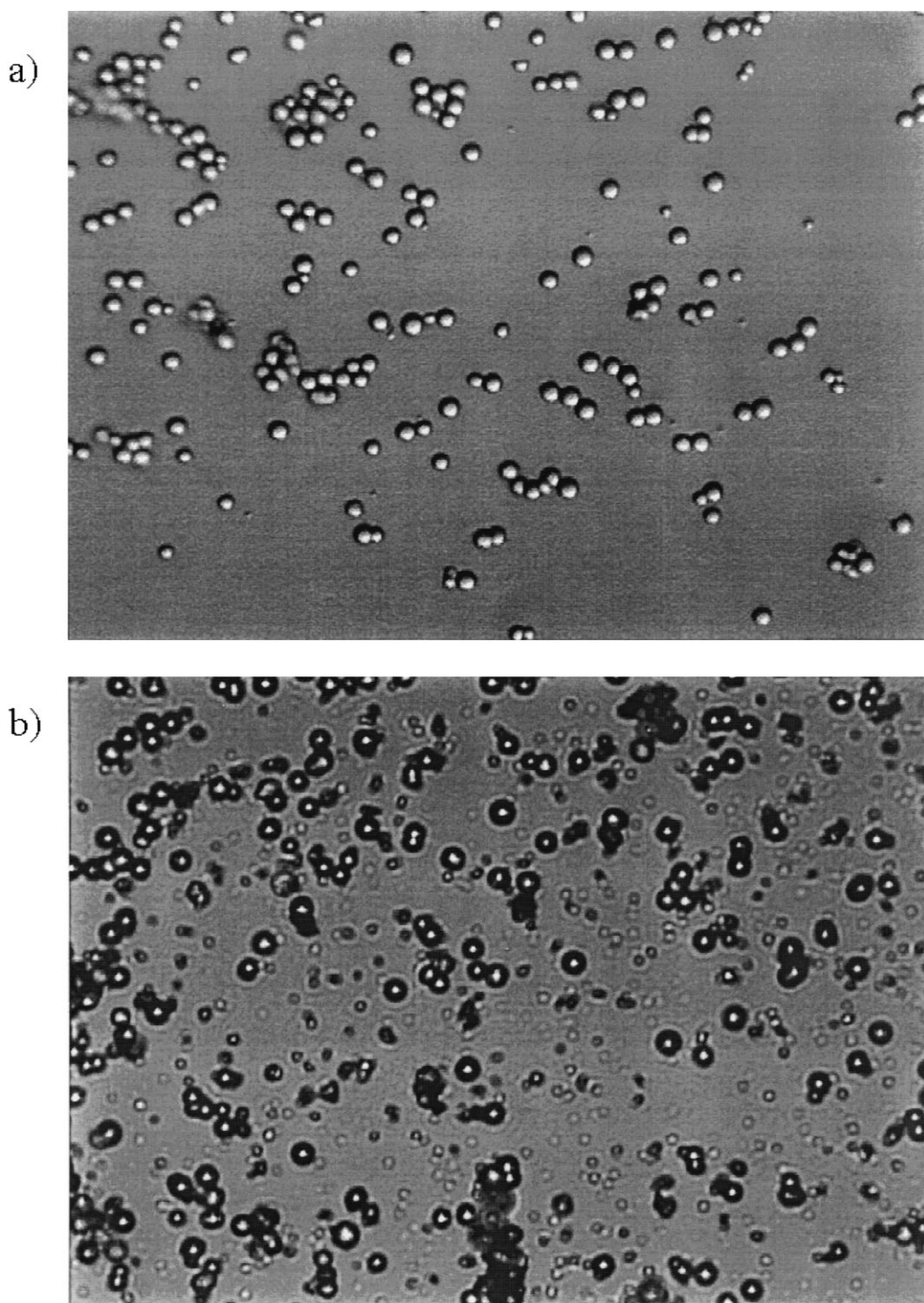


Fig. 2. Micrographs of (a) bare silica gel and (b) silica gel after horizontal polymerization, where the silica had been exposed to 60% humidity prior to reaction.

Table 1
Water coverage, microanalysis result and surface charge density at pH 8 for the four levels of relative humidity

Humidity	Water coverage ($\mu\text{mol}/\text{m}^2$)	% Carbon	σ/F ($\mu\text{mol}/\text{m}^2$)
30%	7 ± 3	13	$>1.8 \times 10^{-7}$
40%	13 ± 0.5	14	1.6×10^{-7}
50%	22 ± 3	22	3.6×10^{-8}
60%	35 ± 2	29	–

tionately low. This is likely due to the formation of oligomers that were washed away. The coverage of reagent silicon atoms, in moles/ m^2 , can be calculated from the percent carbon and the known surface area, S , of the silica gel ($350 \text{ m}^2/\text{g}$) if the mole fractions (X) of octadecyl and methyl groups are known. These mole fractions had previously been determined from ^{13}C NMR spectroscopy to be $\frac{1}{3}$ octadecyl and $\frac{2}{3}$ methyl [9,19]. The reagent coverage, Γ , is calculated as follows.

$$\Gamma = \frac{\{(\%C/100)^{-1} - 1\}^{-1} / (X_{18} \cdot 18 \cdot 12 + X_1 \cdot 12)}{S} \quad (2)$$

The term $\{(\%C/100)^{-1} - 1\}^{-1}$ is approximately equal to $\%C/100$, and it accounts for the fact that the initial weight in the microanalysis includes carbon in addition to silica. Using Eq. (2), the calculated coverage is $10 \mu\text{mol}/\text{m}^2$, which is exactly the coverage expected for the steric limit of methylsiloxane groups [9]. Incidentally, the coverage of $10 \mu\text{mol}/\text{m}^2$ is unrelated to the underlying coverage of silanol groups because there is little attachment to the silica surface, as shown by ^{29}Si NMR spectroscopy [19]. Instead, this high coverage results from the close-pack geometry of trichlorosilanes in a plane, as demonstrated previously from molecular mechanics simulation [9]. The microanalysis thus points to 50% as the closest humidity to the optimum.

NMR studies were not performed on the material prepared at 60% humidity because the interference from the excess polymer would undermine the interpretation. Fig. 3 shows the ^{29}Si NMR spectra for the materials prepared at 30, 40 and 50% humidity. Peak assignments have been previously designated by Sindorf and Maciel [20]. The peaks at -47 ppm

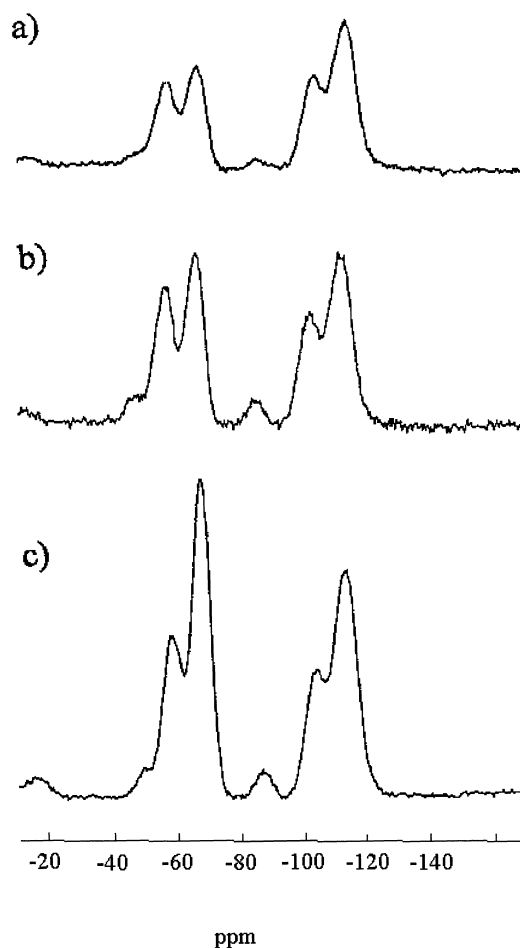


Fig. 3. ^{29}Si NMR of the mixed $\text{C}_{18}\text{-C}_1$ horizontally polymerized monolayers on silica gel prepared after exposing the silica gel to (a) 30%, (b) 40% and (c) 50% humidity, prior to reaction.

and at -59 ppm are due to terminal hydroxyl groups on the reagent; these are indicative of defects in the monolayer. The peak at -69 ppm is due to the desired, fully cross-linked, reagent species. The peak at -88 ppm has only been reported for horizontally polymerized systems, and might be due to strain in the silica surface resulting from the monolayer formation [19]. The monolayers formed using 30% and 40% humidity both show that the signal at -59 ppm from defect sites is comparable to that of the -69 ppm signal from the fully cross-linked sites. The material prepared using 50% humidity displays the greatest amount of cross-linking, where the intensity of the -69 ppm peak is 2.5-times greater

than the peak at -59 ppm. The NMR data thus show that 50% humidity is considerably better than the 30% or 40% levels for preparing extensively cross-linked monolayers.

To probe the exposure of the silica substrate, the chromatograms of $\text{Ru}(\text{bpy})_3^{2+}$ were acquired for the materials made at 30%, 40% and 50% humidity. The material synthesized using 60% humidity was unable to be packed due to excessive backpressure, therefore, it was not studied chromatographically. The backpressure was attributed to the presence of the ~ 1 μm particles, which would increase the backpressure by decreasing the permeability of the column. Fig. 4 shows the chromatograms of 60 mM $\text{Ru}(\text{bpy})_3^{2+}$ for each of the three materials at pH 8. The differences among the three phases are apparent and dramatic. $\text{Ru}(\text{bpy})_3^{2+}$ did not elute from the column packed with the material prepared using 30% humidity over the 22 min time scale of the experiment. For the cases of 40% and 50% humidity, elution occurred at 16 min and 0.8 min, respectively, thus showing a very strong dependence on humidity of the silica in the synthesis. The chromatographic data agree with the microanalysis and NMR data, all pointing to 50% humidity as close to the optimum.

The chromatographic data also allow calculation of the area of exposed silica substrate. Assuming only the electrostatic contribution to the free energy of adsorption changes with pH, and assuming the surface charge density is negligible at pH 2, the electrostatic interaction energy, E , for $\text{Ru}(\text{bpy})_3^{2+}$, at

pH 8 can be calculated for each monolayer, as shown previously [18].

$$E = RT \ln \left(\frac{t_r(\text{pH} = 8) - t_m}{t_r(\text{pH} = 2) - t_m} \right) \quad (3)$$

Gouy–Chapman theory relates this energy to the surface charge density, σ .

$$\sigma = - (8kT\varepsilon\varepsilon_0 I)^{\frac{1}{2}} \sinh(E/2kT) \quad (4)$$

I is the ionic strength, and all variables have their usual meanings in electrostatic theory. Table 1 lists the surface charge densities calculated from the chromatographic data through Eqs. (3) and (4) for the materials made at 30%, 40% and 50% humidity. For bare silica, the molar surface charge density, σ/F , is $8.5 \cdot 10^{-7}$ mol/m² [21,22], which is significantly larger than that for any of the surfaces in question. Only silica exposed to the mobile phase is able to deprotonate [21,22], therefore, the surface charge is proportional to the area of exposed silica. Thus, for case of 50% humidity, the surface charge density indicates that only 4% of silica surface is exposed. This is lower than the percentage of defects indicated in the ²⁹Si NMR spectra, suggesting that conformational disorder of the octadecyl chains provides additional coverage of exposed silica. For the case of 40% humidity, 18% of the silica substrate is exposed. The lower carbon percentage from the microanalysis would predict twice this amount of exposed silica, which again shows that the carbon percentage underestimates the ability of the octadecyl chains to cover the substrate.

For the case of 30% humidity, no retention was observed as of 22 min of observation, after which the zone would be too broad to detect reliably. This is at first surprising, given that the carbon coverage decreases only by 1% compared to that for the case 40% humidity. A 1% change in carbon coverage is the level of noise in microanalysis. One can calculate from Eqs. (3) and (4) how high the surface charge density would have to be to increase the retention time beyond 22 min. The answer is that only a slight increase in surface charge density is needed, from $1.6 \cdot 10^{-7}$ to $1.8 \cdot 10^{-7}$ $\mu\text{mol}/\text{m}^2$, which would require only a 2% increase in the area of exposed silica. Thus, a decrease in %carbon on the order of the noise in the microanalysis would cause the

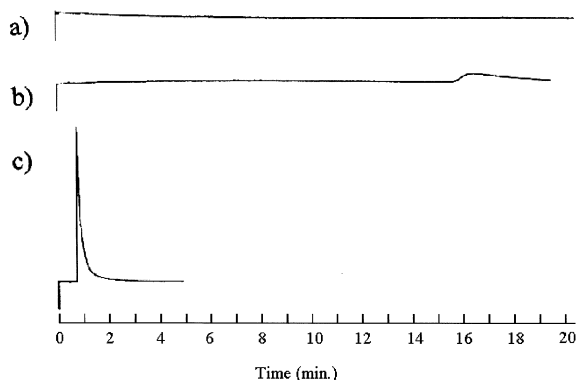


Fig. 4. Chromatograms of $\text{Ru}(\text{bpy})_3^{2+}$ at pH 8 for the mixed C_{18} – C_1 horizontally polymerized monolayers on silica gel prepared after exposing the silica gel to (a) 30%, (b) 40%, and (c) 50% humidity, prior to reaction.

elution to become undetectable. This underscores the high sensitivity of chromatography as a means of probing surface coverage by the monolayer. The high sensitivity of chromatography owes to the fact that retention time increases exponentially with the energy interaction between the analyte and the surface.

4. Conclusions

The amount of adsorbed water on fully hydroxylated silica increases nonlinearly with humidity, requiring control of humidity to achieve dense horizontal polymerization of trichlorosilanes. At room temperature, a relative humidity of 60% gives excess polymer, while relative humidity levels of 30 and 40% give insufficient monolayer coverage of the silica substrate. The optimal 50% humidity corresponds to $22 \pm 3 \mu\text{mol}/\text{m}^2$ of adsorbed water. Finer increments of humidity might resolve a more precise optimum. The optimum represents a 2.5:1 molar ratio of adsorbed water to trichlorosilane, which is slightly lower than the stoichiometric ratio of 3:1. A plausible explanation is that an unreacted chloro group, resulting from incomplete hydrolysis, is more likely to have a hydroxy group as a neighbor than another unreacted chloro group, and this would still allow formation of a siloxane bond. The defects evident in the ^{29}Si NMR spectrum at the optimum humidity may be due, in part, to sites where chloro groups were unable to condense with neighboring hydroxy groups. The optimization involves a balance between providing the requisite amount of water for the hydrolysis and minimizing polymerization of unattached reagent.

Acknowledgements

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