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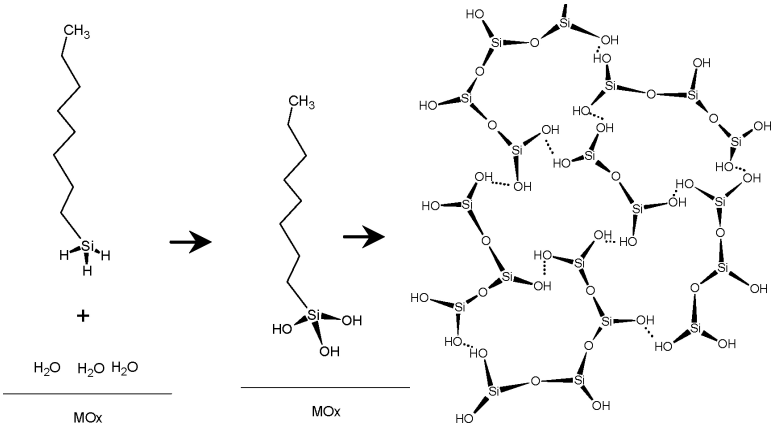

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Reaction of Organosilicon Hydrides with Solid Surfaces: An Example of Surface-Catalyzed Self-Assembly

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Abstract: The solution-phase reactions of octadecylsilane ($C_{18}H_{37}SiH_3$) with 10 high surface area metal oxides (groups II−VIII) were investigated. $C_{18}H_{37}SiH_3$ reacted with most metal oxides at room temperature and produced supported monolayers (self-assembled monolayers, SAMs) with a high grafting density of C_{18}, ∼4.5−5 groups/nm^2. According to the FTIR and ^{29}Si NMR spectra, molecules in the SAMs demonstrated "horizontal" cross-linking (Si−O−Si and Si−OH···HO−Si bonds) and little or no "vertical" bonds with the metal oxide forming an amorphous, yet ordered film. Also, ∼3 mol of H_2 was formed per each mole of grafted C_{18}, indicating complete hydrolysis of $C_{18}H_{37}SiH_3$ during the reaction. On the basis of the activity of different metal oxides, we concluded that the hydrolysis of $C_{18}H_{37}SiH_3$, the key step in the reaction mechanism, is catalyzed by water adsorbed on acidic and basic centers (Lewis and Brönsted) of the surface of metal oxide. Metal oxides and solids with weak acidic and basic properties, like silica, carbon, and organic polymers, do not react with $C_{18}H_{37}SiH_3$. Increasing the temperature of the reaction or doping neutral surfaces with acids or bases greatly increases their activity in the reaction with $RSiH_3$.

Introduction

The covalent modification of solid surfaces is a powerful approach in the designing of materials with a desired level of solid−liquid and solid−vapor interactions. This is of prime interest in sorption and separation, wetting and adhesion, polymer composites, sensors, and other applications.[1−3] Hence, the development of reproducible and versatile synthetic tools for the selective surface modification of different materials is needed.

Organosilanes with the general formula, R_nSiX_{4-n}, where X is a reactive leaving group, have been used for surface modification and as coupling agents for more than 50 years.[1a] Organosilanes with different organic side groups (R), leaving groups (X), and functionalities ($n = 0-4$) are available, which allows for the preparation of a large variety of organosilicon monolayers and thin films.[4] The use of organosilicon hydrides (X = H) in surface modification has several advantages over other silane coupling agents. It provides a clean reaction environment (the byproduct is hydrogen gas) and, thus, simplifies the synthetic procedure. For example, in the reactions of commonly used chloro (X = Cl), *N*,*N*-dimethylamino (X = $N(CH_3)_2$), and methoxy (X = CH_3O) silanes, the byproducts are corrosive and/or highly reactive compounds, HCl, $HN(CH_3)_2$, and CH_3OH, respectively. A clean reaction environment improves the uniformity of the supported thin films and makes the surface modification technique more reproducible.

Perhaps, the first use of organosilicon hydrides (silicones with Si−H groups) for water proofing of construction materials was reported by Andrianov and Sobolevsky[5] in 1949. Voronkov et al. in a series of work[6,7] reported the use of low- and high-molecular weight organosilicon compounds with Si−H groups for water repellency and protective coatings. Although in early publications[5−7] the importance of the presence of the Si−H group in the hydrophobizing agents was emphasized, the structure of the films and the mechanism of the surface binding were not studied in detail. Tada et al. reported[8−10] the reaction of 1,3,5,7-tetramethyl-cyclotetrasiloxane with the surface of TiO_2. The preparation of self-assembled monolayers of $RSiH_3$ supported on metals and metal oxides was described in our work[11,12] and in the work[13−15] of other groups. The present work summarizes our recent data on the reaction of alkylsilanes $RSiH_3$

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(mostly $C_{18}H_{37}SiH_3$) with different metal oxide powders. The structure of the monolayers and the reaction mechanism are discussed.

Experimental Section

General Information. Solvents (HPLC grade) were purchased from Aldrich. Octadecylsilane was purchased from Gelest and used as received. Infrared spectra were obtained with a Perkin-Elmer Spectrum One FTIR instrument with DTGS detector (reflectance mode, 45° angle of incidence, 100 scans, resolution 4 cm^{-1}). Hydrogen analysis was made with an Agilent GC equipped with an RTX M sieve 13X column (30 × 0.53 mm i.d. × 1.0 μm film thickness) operated isothermally at 40 °C for 5 min, inlet temperature of 200 °C, a thermal conductivity detector temperature of 300 °C, and a column flow of 1.2 mL/min. Chemical analysis of supported SAMs was performed by Schwarzkopf Microanalytical Lab (Woodside, NY) using the ASTM method. Grafting density (ρ, group/nm^2) of the SAMs was calculated using the formula:

$$\rho = \frac{6 \times 10^5(\%C)}{[1200 \times n_C - MW \times (\%C)]} \cdot \frac{1}{S(BET)} \qquad (1)$$

MW is the molecular weight of the grafted group, n_C is the number of carbon atoms in the grafted group, %C is the weight carbon percentage in the sample, and S(BET) is the BET (N_2) surface area of bare metal oxide (m^2/g). ^{29}Si SS-NMR (solid-state NMR) experiments were performed on a Bruker DSX-400 NMR spectrometer. The ^{1}H and ^{29}Si resonance frequencies are 400.1 and 79.5 MHz, respectively, at this magnetic field strength. ^{1}H/^{29}Si CPMAS experiments were performed using a Bruker double-resonance, variable-temperature CPMAS probe and a standard variable-amplitude CP pulse sequence using a 2.0 ms contact time. ^{29}Si pulse-acquire experiments utilized a standard pulse-acquire sequence. For all ^{29}Si spectra, 4k of data points were acquired in 60 ms and then zero-filled to 8k before transformation using 100.0 Hz of line broadening. Recycle delays for all experiments were 2.0 s. Rotor frequency was 3.0 kHz. All ^{29}Si spectra were referenced to TMS using Tetrakis as a secondary reference.

Metal Oxides and Their Reaction with Octadecylsilane. The list of metal oxides is presented below. Information about vendor, purity of metal oxide, and BET surface area is given in parentheses. MgO (Aldrich, >99%, 41 m^2/g); ZnO (Aldrich, 99.999%, 8 m^2/g); Al_2O_3 (Aldrich, >99.99%, 41 m^2/g); SiO_2 (Cabot, 99.9%, 150 m^2/g); TiO_2 (Aldrich, >99.9%, rutile, 2.5 m^2/g); TiO_2 (Aldrich, >99.9%, anatase, 11 m^2/g); ZrO_2 (Magnesium Electron, 99.99%, 17 m^2/g); MoO_3 (Aldrich, >99%, 0.7 m^2/g); WO_3 (Aldrich, >99%, 1.6 m^2/g); Fe_2O_3 (Aldrich, 99.998%, 14 m^2/g); NiO (Aldrich, >99%, 0.5 m^2/g). Surface area measurements were performed with a Coulter 100CX instrument using low-temperature nitrogen adsorption. BET surface areas were calculated assuming the cross section for nitrogen[16] is $a(N_2) = 13.5$ Å^2.

The reaction of metal oxides with octadecylsilane ($C_{18}H_{37}SiH_3$) was carried out following the procedure described in ref 12.

Results and Discussion

Structure of the Monolayers of $C_{18}H_{37}SiH_3$ Supported on Metal Oxides. Table 1 shows data for maximal grafting densities for the surfaces prepared by the reaction of $C_{18}H_{37}$-SiH_3 with different metal oxides. All surfaces show high grafting density around ~4.5−5 group/nm^2. Grafting densities in this range have been reported for the SAMs of $C_{18}H_{37}SiCl_3$ and $C_{18}H_{37}P(O)(OH)_2$ on metals and metal oxides,[17,18] $C_{18}H_{37}SH$ on gold,[19] and LB films of fatty acids and alcohols supported on solid surfaces.[20] Molecules in these SAMs occupy an area of ~20−22 Å^2, which is ~10−15% greater than the crystallographic projection of the poly(ethylene) chain in crystals.[21]

Table 1. Properties of Metal Oxides and Supported SAMs of $C_{18}H_{37}SiH_3$

metal oxide	IEP	rate constant of SAM formation (25 °C), L/mol·h	grafting density of C_{18}-SAMs, group/nm^2	$\nu(CH_2)$, cm^{-1}
MgO	12.4	n/d	4.84 ± 0.05	2918
NiO	10.3	13.4 ± 5.5	4.91 ± 0.15	2920
ZnO	9.2−10.3	8.2 ± 1.2	4.92 ± 0.05	2916
γ-Al_2O_3	8−9.6	10.6 ± 1.2	4.33 ± 0.05	2920
ZrO_2 monocl.	7−10	22.6 ± 2.3	4.74 ± 0.05	2918
Fe_2O_3	6.7	22.4 ± 2.3	4.82 ± 0.05	2916
TiO_2 rutile	6−8	15.5 ± 4.5	4.85 ± 0.05	2916
TiO_2 anatase	2	19.5 ± 2.3	4.43 ± 0.08	2917
MoO_3	2.8	9.3 ± 5.5	4.80 ± 0.15	2918
WO_3	0.5	6.6 ± 5.5	4.75 ± 0.15	2920
			average = 4.75 ± 0.08	

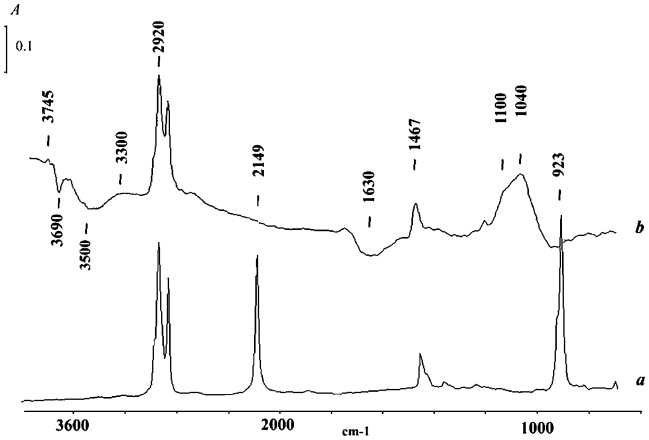

Figure 1. Difference IR spectra obtained for TiO_2 (anatase) after the reaction with $C_{18}H_{37}SiH_3$ (b) and IR spectra of liquid $C_{18}H_{37}SiH_3$ (a).

High values of grafting density indicate the formation of closely packed organic monolayers and suggest ordering in the monolayers. The order in the SAMs of $C_{18}H_{37}SiH_3$ was demonstrated by the position of the CH_2-stretching. For well-ordered SAMs,[22] the CH_2 stretching is close to that of crystalline alkane (ν_a ~2915−20 cm^{-1}), while for disordered structures it is close to that of a liquid alkane[23] ($\nu_a \approx$ 2924−28 cm^{-1}). The data in the table show that $\nu_a(CH_2)$ is in the range 2916−2920 cm^{-1}, indicating the formation of well-ordered SAMs for all metal oxides studied.

The chemical bonding in the SAMs was characterized by FTIR and ^{29}Si NMR spectroscopy. After being reacted with $C_{18}H_{37}SiH_3$, all metal oxides showed very similar IR spectra. The major difference was in band intensities due to differences in the surface area and optical properties of metal oxides. Figure 1 shows a typical difference IR spectra obtained by the subtraction of the bare metal oxide spectra from the spectra of the metal oxide reacted with $C_{18}H_{37}SiH_3$. The following features

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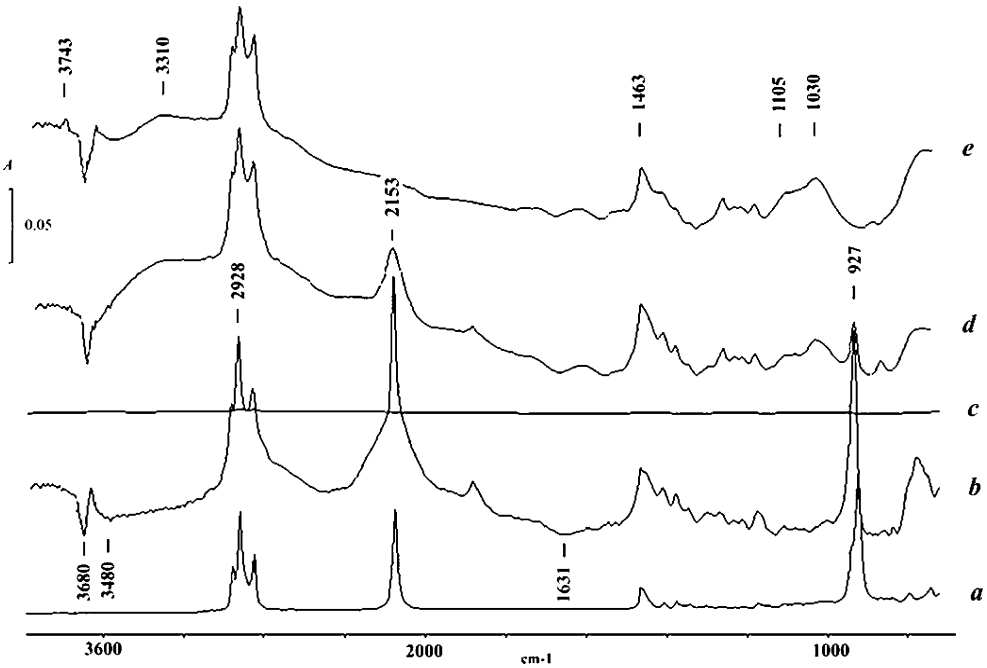

Figure 2. Difference IR spectra obtained for the reaction of $C_8H_{17}SiH_3$ vapors with ZrO_2 dried at 100 °C. (b) After contact with silane vapors at 25 °C for 30 min; (c) sample 2 after evacuation at 10^{-3} Torr for 30 min; (d and e) after contact with silane vapors at 75 °C for 3 and 12 h, respectively. (a) Transmission spectra of liquid $C_8H_{17}SiH_3$.

were present. The negative bands at 3690, ~3500 (broad), and 1630 cm^{-1} were stretching and deformation vibrations of adsorbed water.

The narrow band (~3690 cm^{-1}) was assigned to the stretching of free OH groups from water molecules H-bonded to electron acceptor groups (e.g., H−O−H···O).[24,25] The broad band centered at ~3500 cm^{-1} was assigned to the stretching of the H-bonded OH groups of adsorbed water with the deformation mode at 1630 cm^{-1}.[24−26] Disappearance of these bands from the spectra indicated the removal of molecular water from the surface due to the reaction with $C_{18}H_{37}SiH_3$. The bands at ~2920, 2850 ($\nu(CH_2)$), and ~1470 cm^{-1} ($\delta(CH_2)$) were from *n*-octadecyl groups. An intense broad band with a complex structure at ~1100−1000 cm^{-1} argued for the formation of a siloxane species (Si−O) on the surface. In our previous work,[12] these bands were assigned to a siloxane network (Si−O−Si) supported on the surfaces of the metal oxides. It is noted that the bands at ~920 (δ(SiH)) and ~2150 cm^{-1} (ν(SiH)) were not present in the spectra, indicating complete hydrolysis of the SiH groups of $C_{18}H_{37}SiH_3$ yielding SiO and SiOH.

In-situ IR studies provided details about the reaction of $RSiH_3$ with surfaces. Figure 2 shows the evolution of the difference IR spectra as $C_8H_{17}SiH_3$ vapor reacts with hydrated ZrO_2. The reaction started with the adsorption of octylsilane and its interaction with the adsorbed water, probably via H-bonding. This appeared in the spectra as a decrease of the 3690 cm^{-1} band (free OH groups of water) and a redistribution of the intensities in the 3500−3400 cm^{-1} region (H-bonded water). The chemical reaction between silane and surface water, however, was quite slow at room temperature, and the adsorbed silane could be completely removed by evacuation after 30 min of the adsorption (Figure 2c). At elevated temperature (75 °C), the reaction speeded up significantly and new bands at ~1100−1000 (ν(Si−O) in Si−O−Si) and ~3300 cm^{-1} (ν(OH) in Si−OH) appeared in the spectra, evidence of the hydrolysis and condensation of $RSiH_3$.

As the reaction progressed, the 3300 cm^{-1} band decreased and the 1100−1000 cm^{-1} band increased, indicating condensation of silanols with the formation of siloxanes. It is noted that this condensation did not go to completion. The broad band at 3300 cm^{-1} (H-bonded silanols) and a narrow band at 3745 cm^{-1} (isolated SiOH)[26,27] indicated the presence of noncoupled silanols (Si−OH) even in the monolayers with the close packing of alkyl groups (>4.5 group/nm^2) (Figures 1 and 2).

The presence of both hydrogen-bonded and isolated silanols in the monolayers can be rationalized by steric considerations. In earlier works,[28−32] it was proposed that siloxane (Si−O−Si) cross-links played an important role in the stabilization of monolayers of alkyltrichlorosilanes. An idealized structure of the SAM with the Si atoms located in a hexagonal array and connected via siloxane linkages is shown in Figure 3B. The alkyl chains (not shown in the figure) were directed perpendicular to the plane of the siloxane network. The structure shown in Figure 3B, however, would be too constrained due to the steric repulsion between alkyl chains, which was pointed out in refs 28, 31, and 32. The maximal length of the Si−O−Si bond is 0.32 nm (for the ∠Si−O−Si 180°), which is notably smaller than the van der Waals diameter of the alkyl chains (~0.46 nm). Hence, the formation of an ideally packed cross-linked monolayer shown in Figure 3B is hardly possible because of the space requirements. We believe that the closely packed

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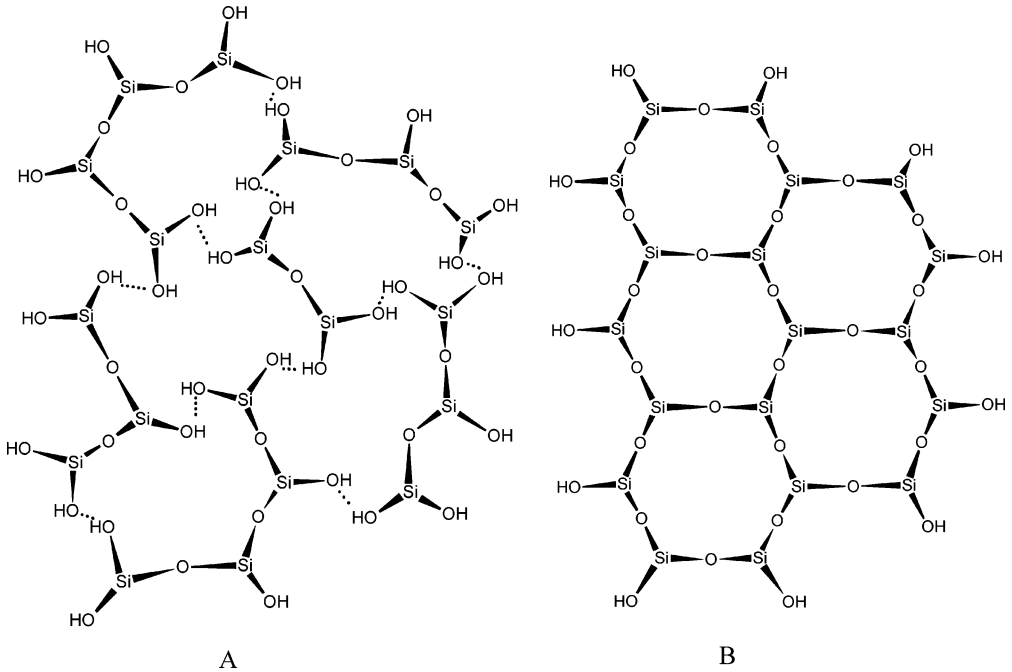

Figure 3. The proposed structures of alkylsiloxane SAMs. Amorphous structure (A) consists of the molecules bonded via Si−O−Si and Si−OH···HO−Si bonds. Crystalline-like structure (B) has "extended" Si−O−Si bonds, proposed in refs 28−32. In both cases, the SAMs are additionally stabilized by the van der Waals interactions between alkyl chains (stretched perpendicular to the plane, not shown).

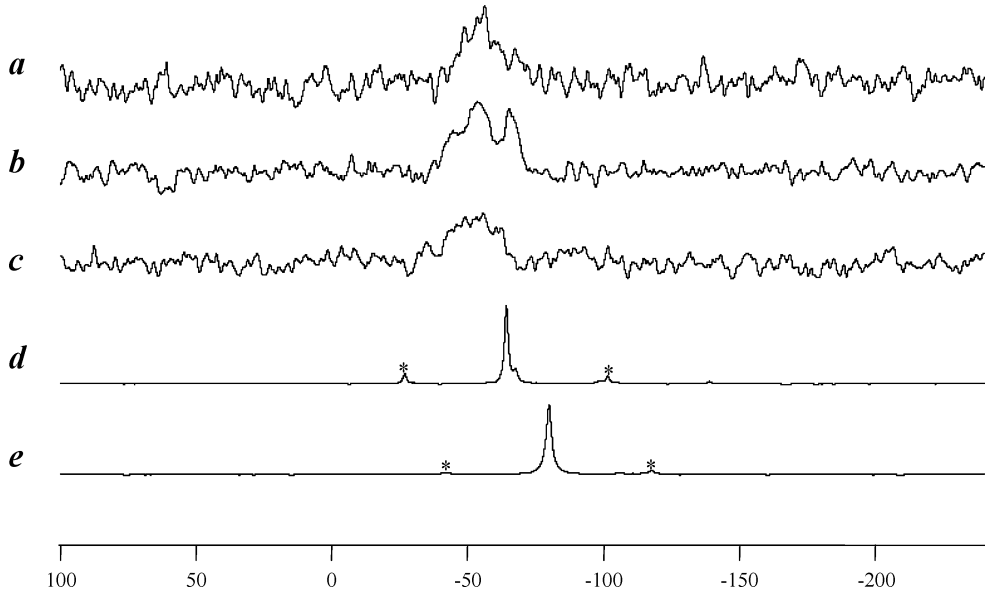

Figure 4. ^{29}Si NMR spectra: $C_{18}H_{37}SiH_3$ monolayers supported on TiO_2 (a); MgO (b); Al_2O_3 (c); octacyclopentyl-T8-silsesquioxane (reference for Si−O−Si) (d); and $ZrSiO_4$ (reference for metal−O−Si) (e). Spectra a−c utilized CPMAS, 20k acquisitions. Spectra d and e utilized pulse-acquire; both spectra had 128 acquisitions.

SAMs form an ordered yet amorphous film with a significant number of the uncoupled Si−OH groups that interact with neighboring Si−OH groups via hydrogen bonding as shown in Figure 3A. The presence of the Si−OH groups in the monolayer will provide the required space for the alkyl chains, as the maximal length of the Si−OH···HO−Si sequence of bonds is ∼0.6 nm. The whole integrity of the structure shown in Figure 3A is provided by a system of hydrogen bonds (Si−OH···HO−Si and, perhaps, M−OH···HO−Si) and van der Waals interactions between the alkyl chains. The structure in Figure 3A is supported by the X-ray diffraction study,[33] where the C_{18} SAMs were shown to form a distorted hexagonal lattice with no long-range order and an area per molecule of 20.2 Å^2.

SS-NMR data were in good agreement with the FTIR data and also supported the formation of an amorphous free-standing siloxane film, which is not directly bound to the surface of metal oxides. The ^{29}Si CPMAS spectra for SAMs supported on different metal oxides (Figure 4a−c) were similar to each other and displayed a broad peak (centered ∼ −60 ppm) with possibly two unique ^{29}Si sites. The spectrum from a solid reference of a Si−O−Si linkage (solid T8-silsesquioxane, Figure 4d) displayed two sharp ^{29}Si peaks (−64 and −68 ppm) representing two distinct crystallographic ^{29}Si sites in a crystalline material.[34] The spectrum from the solid reference of an M−O−Si linkage

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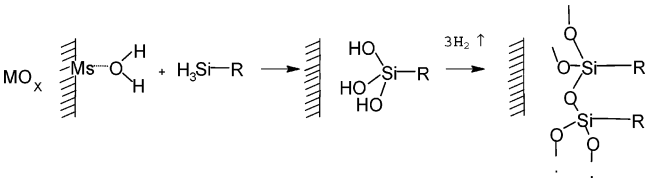
displayed one sharp ^{29}Si peak (~ −80 ppm for Zr−O−Si, Figure 4e) representing one crystallographic ^{29}Si site in a crystalline material. Comparing chemical shift values of the bound Si spectra to solid references, it was clear that the SAMs demonstrated Si−O−Si linkages and no Si−O−M linkages. The ^{29}Si peaks in the SAMs were significantly broadened as compared to the standard solid Si−O−Si and M−O−Si reference spectra. This peak broadening is most likely due to the amorphous character of the silicon atoms in the SAMs. Amorphous materials yield broad SS-NMR peaks due to the distribution of isotropic peaks.[35]

The data on grafting density (Table 1), along with the spectral changes observed by FTIR and NMR spectroscopy, suggested that the major product of the reaction of $C_{18}H_{37}SiH_3$ with the surface was independent of the nature of metal oxides and presented densely packed amorphous alkylsiloxane networks stabilized through "horizontal" Si−O−Si and Si−OH···HO−Si bonds (Figure 3A). Although the integrity of these SAMs is mostly determined via lateral interactions rather than through bonding to the substrate, the stability of these surfaces is impressive. The hydrolytic stability of the $C_{18}H_{37}SiH_3$ SAMs supported on TiO_2 and ZrO_2 was reported[36] to be in the range of pH 1−10 at 25 °C, and the thermal degradation of these SAMs did not start until 180−200 °C (in air) and ~300 °C (in N_2).[12]

Mechanism of Self-Assembly. The reaction of $C_{18}H_{37}SiH_3$ with hydrated metal oxides produces hydrogen gas. About 3 mol of hydrogen (H_2) is released per mole of grafted C_{18} chain. In our previous work,[11] this was demonstrated for TiO_2. In this work, it was proven for all metal oxides listed in Table 1. The stoichiometry 3:1 agrees with the complete hydrolysis of $C_{18}H_{37}SiH_3$ during the reaction with metal oxides. We found, however, that $C_{18}H_{37}SiH_3$ showed virtually no hydrolysis by air moisture or wet organic solvents under the reaction conditions employed. From organosilicon chemistry, it is known that hydrolysis of the Si−H bonds in alkylsilanes requires a catalyst, typically acids and bases.[37]

To evaluate the role of the metal oxide, we investigated the kinetics of the reactions of $C_{18}H_{37}SiH_3$ with metal oxides spanning the range of surface acidity and basicity. The acid−base properties of the metal oxides were characterized by their isoelectric points (IEP)[43] (Table 1). The kinetics of the surface reactions was studied at room temperature using two techniques: (1) directly by measuring the amount of H_2 released during the reaction, and (2) indirectly by chemical analysis (C,H) of the metal oxides reacted with $C_{18}H_{37}SiH_3$ over a certain time period. The results obtained by these two techniques were essentially the same. The kinetic data were characterized by two distinct first-order processes. The initial process (rate constant k_1) is a relatively rapid growth in grafting density followed by a slow period (rate constant $k_2 \approx 0.01 \cdot k_1$), during which surface coverage approaches its final value. The uptake curves were approximated by two exponential functions: $\theta/\theta_0 = 1 - \alpha e^{-k1Ct} - \beta e^{-k2Ct}$, where $\alpha + \beta = 1$, θ is the grafting density at time t, θ_0 is the maximum grafting density, and C is the concentration of $C_{18}H_{37}SiH_3$ in solution. The parameters k_1, k_2, and α were obtained through a curve-fitting procedure. The rate constants of the initial process of the monolayer growth (k_1) are shown in Table 1.

Scheme 1. Hydrolysis of $RSiH_3$, the Key Step in the Surface Self-Assembly, Is Catalyzed by Water Adsorbed on Acidic or Basic Centers (Lewis or Brönsted) on the Surface



Analysis of the kinetic data in Table 1 demonstrates that (1) there seems to be no correlation between the reaction rates and the IEP of metal oxides, and (2) $C_{18}H_{37}SiH_3$ reacts with all metal oxides at comparable rates, yielding organic surfaces of the same quality. Not all solids, however, react with $C_{18}H_{37}SiH_3$. We found that fume silica (aerosil) and silica gels, carbon black, and organic polymers (poly(ethylene), poly(ethyleneterephthalate), and others) do not react with $C_{18}H_{37}SiH_3$. No grafting of alkylsilane to the surface or release of hydrogen was detected even after an extended reaction time. On the basis of the activity of different surfaces, we concluded that only metal oxides with ionic character are active in the reaction with $C_{18}H_{37}SiH_3$. The presence of unsaturated metal ions, hydroxyl groups, and oxygen anions determines the presence of strong acid−base centers (Lewis and Brönsted) on the surfaces of metal oxides.[44,45] We believe that the reaction of hydrolysis, the key step in the reaction of $RSiH_3$ with the hydrated surfaces, is catalyzed by acidic or basic centers on the surface (Scheme 1). The reaction mechanism includes hydrolysis of $C_{18}H_{37}SiH_3$ by surface water followed by assembly of $C_{18}H_{37}Si(OH)_3$ into a cross-linked siloxane network (Si−O−Si and Si−OH···HO−Si linkages) supported by the surface of the metal oxide.

The mechanism proposed above is similar to that proposed for the self-assembly of $RSiCl_3$ on hydrated surfaces.[38−40] It is noted, however, that there are at least two fundamental differences in the self-assembly of $RSiCl_3$ and $RSiH_3$: (1) the role of solid and (2) the role of water in the reaction. In the case of $RSiCl_3$, the nature of the solid seems to be irrelevant as long as the substrate provides a hydrous interface for the reaction. SAMs of the same quality can be prepared on such different surfaces as silica,[30] mica,[28,41] gold,[42] and OH-terminated organic monolayers.[30] In the case of $RSiH_3$, the nature of the solid is critical because it participates in the reaction as a catalyst. Only solids with acidic or basic sites on the surfaces are active. Next, $RSiCl_3$ is readily hydrolyzed by water in solution and by atmospheric moisture. The excess of water in the reaction system causes uncontrollable polycondensation of trichlorosilanes and affects

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the quality of the SAMs. Opposite to $RSiCl_3$, $RSiH_3$ (for R > C_8−C_{10}) are quite stable and show little or no hydrolysis or oxidation (at room temperature) when exposed to air or moisture.[12] Moreover, we have found that an excess of adsorbed water inhibited the self-assembly of $RSiH_3$. The reaction of $RSiH_3$ with metal oxides saturated with water vapors produced organic surfaces of very low grafting density (<0.5 group/nm^2). This can be explained by a polymolecular layer of adsorbed water which blocked the acidic and basic centers of the metal oxide preventing hydrolysis and, hence, the self-assembly of $RSiH_3$.

Covalent metal oxides and solids, like silica, carbon, and organic polymers, show surfaces with homopolar character and exhibit rather weak acid−base properties as compared to the metal oxides with ionic character.[44,45] The absence of strong Lewis and Brönsted centers explains the low activity of these solids in the reaction with $RSiH_3$. In general, the strength of surface acids is determined by the chemical nature of the metal cation (electronegativity, charge, and size) and the local arrangements of the atoms (coordination number); however, no quantitative scale for the acidity of solids is available. We found no correlation between the reaction rates (or any other properties of SAMs) and the acidic or basic properties of the metal oxides as assessed by the IEP or pK_a of surface OH groups.[43−47] This is not surprising as it probably reflects the fact that neither the IEP nor the pK_a completely characterizes the acid−base properties of the surfaces. For instance, the IEPs of silica and titania (anatase) have close values (∼2), but titania readily reacts with $RSiH_3$ at room temperature and silica does not. The activity of titania is explained by the Lewis acid centers present on the surface. Doping of the silica surface with titania by reacting with $Ti(OC_2H_5)_4$ greatly increases its activity. We also found that the reactivity of organosilicon hydrides greatly increases with temperature. For example, silica became active in the reaction with $C_{18}H_{37}SiH_3$ at ∼180 °C. The SAMs obtained at high temperatures, however, were characterized by lower grafting densities (∼3−3.5 group/nm^2) and a lesser order than SAMs obtained at room temperature.

We point out that the hydrolytic self-assembly studied in this work is, perhaps, the most common, but not the only, pathway for the reaction of $RSiH_3$ with surfaces. $RSiH_3$ also reacted with rigorously dehydrated metal oxides that contained no adsorbed water.[12] We believe that these reactions involved the oxidation of $RSiH_3$ into $RSi(OH)_3$ by chemisorbed oxygen. Silanes with small or with no organic group (SiH_4, Si_2H_6, CH_3SiH_3, etc.) react with surfaces via decomposition of silanes and formation of silicon oxide films, which is widely used in CVD technologies.[48]

To conclude, self-assembly of $RSiH_3$ on the surface of hydrated metal oxides is catalyzed by the water adsorbed onto acidic and basic sites (Lewis and Brönsted) of the metal oxide. The major product of the reaction presents a densely packed (∼4.5−5 groups/nm^2) amorphous alkylsiloxane network stabilized by lateral Si−O−Si and Si−OH···HO−Si bonds and supported by the surface. The catalytic role of the solid sets the reaction of $RSiH_3$ apart from the surface reactions described previously, for example, SAMs of $RSiCl_3$, RSH, $RP(O)(OH)_2$, and others. The unique activity of the acid−base surfaces in the reaction with $RSiH_3$ can be used for the selective modification of chemically heterogeneous surfaces, nano-patterning, and other applications.

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