Articles

Effect of Curvature on the Packing and Ordering of Organosilane Monolayers Supported on Solids

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Received March 27, 2007. Revised Manuscript Received November 8, 2007

This work investigated the effects of the nanometer-sized curvature of the substrate on the structure of organic monolayers supported on dispersed and porous solids. A series of covalently attached monolayers (CAMs) was prepared via solution-phase reactions of $C_nH_{2n+1}Si(CH_3)_2N(CH_3)_2$ ($n = 1$–30) with well-defined silicas having (1) convex (fumed silicas) and (2) concave (SBA-15 silicas) surfaces and (3) silicas with nearly flat surfaces (large-pore silica gels). According to chemical analysis and Fourier transform IR, the grafting density and molecular ordering [assessed from the $\nu_a(CH_2)$] in CAMs were largely determined by the steric effects: the concave surfaces hindered while the convex surfaces assisted the formation of closely packed and highly ordered CAMs. The low-temperature adsorption of nitrogen was studied, and the energies of adsorption interactions of CAMs were evaluated using the C constant of the Brunauer−Emmett−Teller equation. For CAMs of intermediate and long alkyl chains ($n > 8$), the grafting density increased, the molecular ordering improved, and the energy of adsorption interactions decreased in the following range of substrates: concave surface−flat surface−convex surface.

Introduction

The use of organosilanes is a powerful and versatile approach in the surface functionalization of minerals and the preparation of solid-supported organic monolayers and thin films.[1–3] Among a great variety of organosilanes used for surface functionalization, monofunctional organosilanes (R_3SiX) having only one hydrolyzable group ($X = Cl$, OR, NR_2, OH) are superior in terms of reproducibility because only one type of reaction with the surface is possible: *covalent attachment* via M_S-O-Si bonds.[3–5] Silica is arguably one of the most important substrates, and a great deal of work on the reactions of monofunctional silanes and, specifically, *n*-alkyldimethylsilanes with silica has been published. Three types of substrate geometries have been the focus of the research: convex surfaces of fumed silicas[6,7] (silica colloids, fillers, and pigments), concave surfaces of porous silicas[8,9] (adsorbents and chromatographic stationary phases), and planar silica surfaces[3,10,11] (adhesion and wetting control). For fully hydroxylated smooth silica surfaces (radius of curvature >> size of grafted molecules), the substrate has little to no effect on the organization of covalently attached monolayers (CAMs). The grafting (packing) density in the monolayers is primarily controlled by the cross-sectional area of the grafted molecules.[6,12] The situation, however, changes for monolayers supported on highly curved surfaces of dispersed and/or porous substrates, with a radius of curvature of a few nanometers. In this case, the geometry of the substrate may influence the packing and molecular ordering in the monolayers, thus affecting adsorption, wetting, and other surface-related properties of the materials. In the literature, the effect of surface curvature on the monolayers was theoretically examined only for the concave surfaces,[13,14] and the results were tested for CAMs supported on porous silica gels.[13,14] Although the models[13,14] adequately described the decrease in the monolayers' grafting density observed in the narrow-pore samples, an accurate evaluation of the pore curvature effects was difficult because

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10.1021/cm070842y CCC: $40.75

Table 1. Characteristics of Silicas As Determined from Nitrogen Adsorption (77 K) and TEM

silica (vendor)	average particle size, μm	S_{N_2}(BET), m^2/g	V_{pore}, cm^3/g	R_{pore}, nm	radius of surface curvature R_C, nm
fumed silica 70 (Aldrich)	0.007	280			−3.5
Aerosil 200 (Degussa)	0.012	170			−6
SBA-24/80[a]	2–3	570	0.64	2.5	2.5
SBA-48/80[a]	2–3	660	0.97	3	3
silica gel Jupiter (Phenomenex)	4–6	170	1.51	17	17
silica gel Davisil 663 (Supelco)	10–15	70		25	25

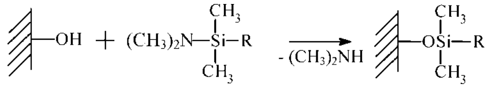
[a] SBA silicas were homemade using the procedure[16] with Pluronic 123 as a surfactant. The first number in the notation is the aging time (h) and the second the aging temperature (°C).

of the complex structure of silica gel pore surfaces, which include concave as well as convex areas.[15] To the best of our knowledge, the case of convex substrates and the role of the substrate curvature on the monolayers' ordering and adsorption properties have not been addressed at all. In the present work, we systematically investigated the effects of the alkyl chain length and surface curvature on the packing, ordering, and adsorption properties of CAMs of alkyldimethylsilanes supported on silicas with well-defined concave, convex, and smooth surfaces.

Materials and Methods

Silicas. Silicas used in this study are listed in Table 1. Specific surface area (S_{BET}, using $a_{N_2} = 0.135$ nm^2) pore volume (determined from the amount adsorbed at $p/p_0 = 0.9$), and pore radius data for bare silicas were obtained from nitrogen adsorption (77 K, Coulter 100CX). The pore radius was obtained as the maximum of the pore-size distribution curves derived from the desorption part of the isotherm using the Kelvin equation. An analysis of the comparison plots (α−*s* plots) demonstrated that all of the samples were essentially free from the micropores.

Preparation of CAMs. Surface modification of silicas was performed using (*N*,*N*-dimethylamino)alkyldimethylsilanes ($C_nH_{2n+1}Si(CH_3)_2N(CH_3)_2$; $n = 1$–30) according to the following scheme:



$$\text{—OH} + (CH_3)_2N\text{—}\overset{CH_3}{\underset{CH_3}{Si}}\text{—R} \xrightarrow[-\,(CH_3)_2NH]{} \text{—O}\overset{CH_3}{\underset{CH_3}{Si}}\text{—R}$$

We used the reaction conditions optimized in our previous work.[4] Similar conditions were also used by Kováts et al.[10] Briefly, prior to the reaction, silicas were dried at 100 °C for at least 3 h. Aminosilane was added to the dried silica in a vial in an amount sufficient to completely cover the sample. C_{18}, C_{20}, and C_{30} silanes were solid at room temperature and had to be preheated before the addition. The vial was then sealed and stored at 60 °C for at least 24 h. The modified silica was placed on a glass filter, washed first with toluene, then acetone, a 3:1 acetone/water mixture (3×), and finally acetone again, and dried at 60 °C for 3 h. Silanes with $n =$ 1, 8, and 18 (Gelest) and $n = 4$ (Aldrich) were used as received. Silanes with $n = 2$, 3, 5–7, 10, 12, 14, 16, and 20 were synthesized in two steps (all chemicals were purchased from Aldrich). (1) Hydrosilation of alkenes with dimethylchlorosilane: 20 mL of dimethylchlorosilane and ∼10 mg of a chloroplatinic acid catalyst were placed in a nitrogen-purged round-bottomed flask and gently heated while 0.85 mol equiv of the appropriate alkene was added dropwise over a period of 2 h; upon addition, the solution was allowed to reflux for 1 h. Subsequent distillation yielded alkyldimethylchlorosilane ($C_nH_{2n+1}Si(CH_3)_2Cl$). (2) Synthesis of (*N*,*N*-dimethylamino)silanes: ∼10 mL of alkyldimethylchlorosilane was dissolved in 100 mL of pentane and saturated with dimethylamine gas (∼10-fold excess by moles). Filtration of the $(CH_3)_2NH\cdot HCl$ salt and removal of the pentane provided the desired (*N*,*N*-dimethylamino)alkyldimethylsilane. Triacontyldimethyl(*N*,*N*-dimethylamino)silane ($n = 30$) was prepared from triacontyldimethylchlorosilane (Gelest).

The progress of surface reactions was monitored using Fourier transform IR (FTIR) and chemical analysis. FTIR measurements were performed using a Perkin-Elmer Spectrum One instrument equipped with a Harrick Seagull reflectance accessory (45° angle of incidence), a mercury−cadmium−telluride detector, 124 scans, and 1 cm^{-1} resolution. Chemical analysis (C and H) of the surface-modified silicas was performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY) using the ASTM method. The grafting density (ρ, groups/nm^2) of the CAMs was calculated via the following equation:

$$\rho = \frac{6\times10^5\,(\%\ \mathrm{C})}{1200n_C - \mathrm{MW}\,(\%\ \mathrm{C})}\,\frac{1}{S(\mathrm{BET})} \qquad (1)$$

where % C is the percent carbon (w/w) in the sample, n_C is the number of carbons in the grafted group, MW is the molecular weight of the grafted group, and *S*(BET) is the Brunauer−Emmett−Teller (BET) surface area of bare silica. For the silicas with large surface areas (∼200 m^2/g and higher), the standard error in the grafting density determination was determined as ±0.01 group/nm^2 or better (based on quintuple repetitive analysis for three different samples).

Determination of Surface Silanols. Determination of the residual (unreacted) surface silanol groups (Si_SOH) in modified silicas was done through the isotope exchange with CD_3OD followed by ^{1}H NMR analysis of the solution (Bruker 300 MHz). All of the glassware used for the analysis was pretreated with (*N*,*N*-dimethylamino)trimethylsilane in order to minimize the contribution from the glass surface silanols and the adsorbed water. Approximately 0.2 g of modified silica was accurately weighed into a headspace vial and subsequently heated at 120 °C for 3 h under vacuum. After the sample was allowed to cool under a passive flow of nitrogen, 2 mL of CD_3OD was injected into the vial and the contents were left to stand for 1 h, which was determined to be sufficient time to reach the proton exchange equilibrium. A total of 20 μL of chloroform was then added via syringe, obtaining the exact amount transferred via weighing. An aliquot was then transferred to an NMR tube prerinsed with CD_3OD and dried under nitrogen. Two prominent peaks were evident in the ^{1}H NMR spectrum, a singlet from the chloroform at 7.8 ppm and a singlet from the methanol hydroxyl group at 4.8 ppm. Integration of the OH peak relative to the internal chloroform standard enabled the calculation of residual surface silanols in the sample. The total amount of silanol groups in bare silica was obtained after summation of the residual silanol groups and the grafting density of alkylsilane. The results are shown in Table 2.

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(15) Silica gels are formed by spherical particles (primary silica particles), and in the first approximation, the surfaces of the pores present areas of convex and concave (around points of contacts) surfaces with varying curvature; see ref 18 for more details.

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Results and Discussion

Selection of Substrates. Three categories of silica substrates with well-defined surface geometry were selected for this study: (1) fumed silica (convex surface of spherical particles); (2) highly ordered mesoporous silicas SBA-15 (concave surface of cylindrical pores), and (3) hydrothermally treated marcoporous silica gels (smooth, nearly flat surfaces of large pores). Although the surfaces of macroporous silica gels were not truly flat, we believed that the effects of the surface curvature on the grafting density were rather small because the radius of curvature (~20 nm) was about 1 order of magnitude greater than the size of the grafted molecules. Also, prior to the reactions with silanes, silicas were subjected to prolonged hydrothermal treatment (boiling in water), which is known to reduce the surface roughness and produce smooth, uniform surfaces.[18] For fumed silicas and SBA-15 silicas, the simple geometry of the surfaces was additionally confirmed by transmission electron microscopy (TEM; Figure 1). Two samples of silica from each category were studied; their characteristics are summarized in Table 1. The concentration of surface silanol groups was determined for silicas from each category using the isotope exchange method. The results are shown in Table 2. We note that while the silicas were of different origin and varied in their particle size, surface area, and porosity, they all showed similar concentra-

Table 2. Determination of Surface Silanols in Modified Silicas

modified silica	unreacted OH groups in the sample, group/nm^2	grafting density of alkylsilane, group/nm^2	total OH groups, group/nm^2
Davisil C1	2.4	2.8	5.2
Davisil C4	4.6	2.1	6.7
Davisil C5	3.2	2.2	5.4
Davisil C8	2.7	2.3	5.0
			average 5.6 ± 0.4
SBA-48/80 C4	3.4	2.2	5.6
SBA-48/80 C8	2.5	2.1	4.6
SBA-48/80 C12	2.8	1.7	4.5
SBA-48/80 C18	3.3	1.7	5.0
			average 4.9 ± 0.2
Aerosil 200 C5	3.0	2.4	5.4
Aerosil 200 C6	2.4	2.4	4.8
Aerosil 200 C7	3.2	2.1	5.3
Aerosil 200 C18	2.5	2.3	4.8
			average 5.1 ± 0.2

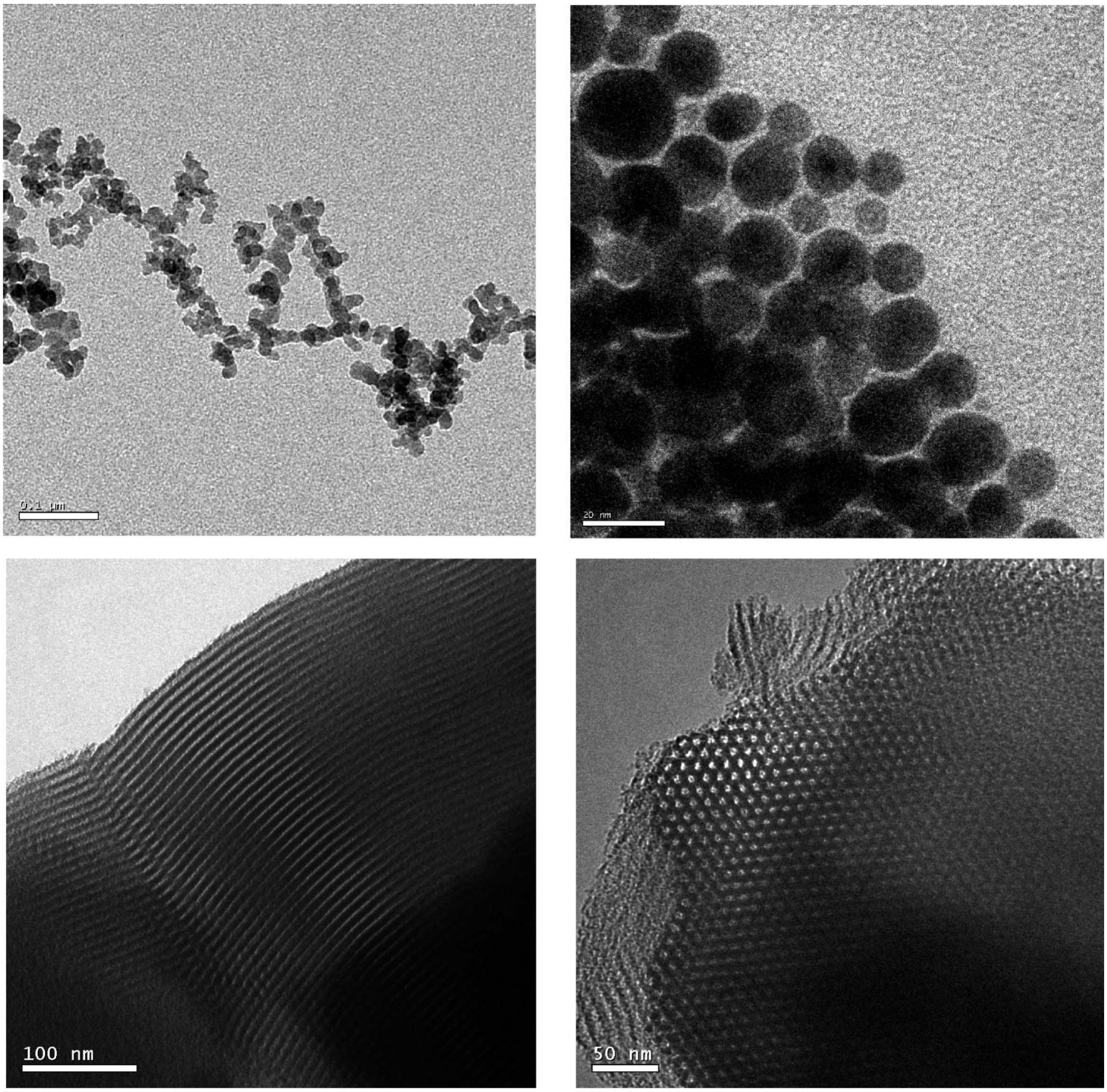

Figure 1. Gallery of TEM images of silicas. Top: Aerosil 200 (scale bars: 100 and 20 nm, respectively). Bottom: SBA-24/80 (scale bars: 100 and 50 nm, respectively).

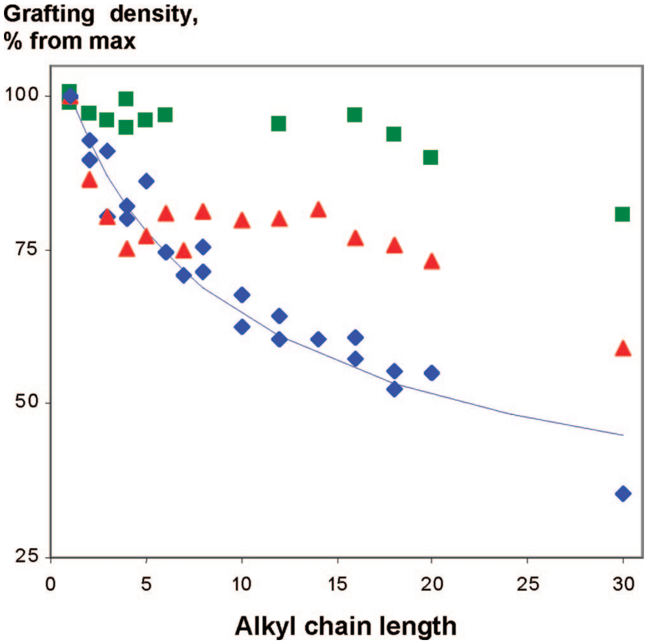

Figure 2. Grafting density as a function of the alkyl chain length for CAMs supported on fumed silicas (squares), SBA-15 silicas (diamonds), and Davisil and Jupiter silica gels (triangles). The dashed line indicates the model calculation (grafted molecules were approximated as rigid balls with the volume equal to the molar volume of liquid alkylsilanes). Vertical dimensions of the symbols represent the standard error in the grafting density.

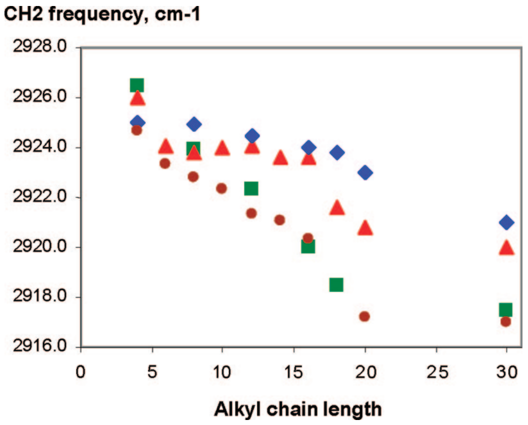

Figure 3. Frequency of the CH_2 stretching (ν_a) as a function of the alkyl chain length for CAMs supported on fumed silica, $R = 3.5$ nm (squares), SBA-15 silica, $R_{pore} = 2.5$ nm (diamonds), and Davisil silica, $R_{pore} = 25$ nm (triangles), and neat alkylsilanes (circles).

tions of silanols, around 5 OH groups/nm^2, which is characteristic of a fully hydroxylated silica surface.[17] Because the concentrations of surface silanols were similar, the differences in the grafting density, molecular ordering, and adsorption properties of CAMs supported on different silicas (see below) were attributed purely to the effects of the surface curvature.

Grafting Density and Molecular Ordering in CAMs. The first important observation was related to the CAMs prepared from (*N*,*N*-dimethylamino)trimethylsilane, the smallest trialkylsilane. The trimethylsilyl CAMs showed grafting densities of ~2.5–2.8 groups/nm^2 for all of the silicas listed in Table 1. It is noted that the value of 2.8 groups/nm^2 (~0.35 nm^2 per molecule) is a maximal possible grafting density, which is attributed to the closest packing of trimethylsilyl groups on silica.[6,12] Therefore, the reaction of trimethylsilane produced the close-packed CAMs of trimetylsilyl groups regardless of the substrate geometry. For the CAMs of longer alkyl chains, however, the effect of the substrate geometry on the CAM structure was quite apparent (Figure 2). The data in Figure 2 suggested three patterns of the chain length dependence for CAMs supported on convex, concave, and nearly flat silica surfaces, respectively. The data for each type of substrate are analyzed separately below.

Nearly Flat Surfaces. For flat silica surfaces, e.g., silicon wafers, glass plates, quartz crystals, and large-pore silicas, the grafting density and ordering of CAMs are functions of the alkyl chain only. The grafting density of CAMs showed a notable decrease when the alkyl chain was increased by a few carbon atoms (from methyl to butyl), while a further increase of the chain length showed little or no effect (Figure 2). For CAMs with $n > 4$, the grafting density leveled off at ~75% from the maximal value observed for the CAM of trimethylsilyl groups. The results obtained here were in very good agreement with the data published for the alkyldimethylsilane CAMs supported on silicon wafers and large-pore silicas.[19–21] The decrease in the grafting density for the short-chained CAMs was attributed to the steric repulsion of the alkyl groups of the increasing size (increased molar volume and cross-sectional area). In order to evaluate the effect of the increasing size of the molecules, the relationship between the grafting density and the molar volume of grafted groups was obtained using the rigid-sphere model of CAMs. In this model, the volume of each sphere was equal to the molecular volume of grafted molecules (V_m). The distance between contacting spheres was $L = 2[(3/4\pi)V_m]^{1/3}$. Assuming hexagonal close packing of molecules in CAMs, the grafting density was obtained as $\rho = 2(3^{1/2}L^2)$, which after the cancelations reduced to $\rho = 0.75V_m^{-2/3}$. Figure 2 (dashed line) shows a plot of the grafting density versus chain length for alkyldimethylsilane CAMs obtained using V_m from the density of alkylsilanes. The agreement between the experiment and the model was quite good for CAMs with chain lengths of up to six or seven carbon atoms. For longer alkyls, however, the experimental grafting density was notably higher than predicted by the model arguing for deviation from the rigid-ball models due to possible orientation and structuring of the long-chained CAMs. We speculate that the increase in the grafting density of the long-chained CAMs was attributed to the increased van der Waals attraction (per mole) between alkyl groups. An increased attraction between alkyls along with higher flexibility of longer chains produced more efficient packing and more ordered structures as compared to the short-chained CAMs.

The molecular ordering in CAMs was assessed by FTIR from the position of the CH_2 stretching of alkyl groups.[22–24]

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For a disordered structure, the frequency of the asymmetric CH_2 stretching is $\nu_a \sim 2928$ cm^{-1}. For well-ordered structures, e.g., self-assembled monolayers (SAMs) of alkylthiols on gold and crystalline alkanes, the frequency is $\nu_a \sim$ 2915–2918 cm^{-1}. Figure 3 presents the $\nu_a(CH_2)$ for a series of CAMs supported on different silicas plotted as a function of the alkyl chain length. For CAMs supported on large-pore silica gels, the frequency shifted from ~2926 cm^{-1} ($n = 4$) to 2923–2924 cm^{-1} ($6 < n < 16$) and further down to ~2920–2921 cm^{-1} (n = 18–30). These data indicated a definite increase of ordering in CAMs with the chain length. We note, however, that the $\nu_a(CH_2)$ in CAMs were always higher than those in the corresponding alkylsilanes (liquids for n = 1–16, solids for $n > 18$ at 20 °C; Figure 3). This suggested that molecules in CAMs were in the state of greater disorder than neat alkylsilanes. The relatively more disordered state of CAMs as compared to neat silanes was attributed to poor lateral contacts between grafted molecules and to the absence of "vertical interactions" for molecules in CAMs.

Concave Surfaces. The grafting density of CAMs supported inside pores of the SBA-15 silicas ($R_{pore} = 2.5$ and 3 nm) showed a continuous decrease with the alkyl chain length (Figure 2). For short-chained CAMs, the decrease was similar to that observed for CAMs supported on large-pore silicas. For long-chained CAMs ($n > 8$), the grafting density did not level off but continued to decrease in a close agreement with the rigid-balls model. The long-chained CAMs supported on SBAs were ~20–25% less densely packed than the Davisil- and Jupiter-supported CAMs of comparable chain length. The decreased grafting density in the CAMs was attributed to the additional sterical constraints for molecules inside narrow cylindrical pores ($R_{pore} \sim 2.5$ and 3 nm) as compared to the flat surfaces. The $\nu_a(CH_2)$ frequency data indicated disordered structures of CAMs corroborating the low grafting density data. Even for the long-chained CAMs (n = 18 and 20), the $\nu_a(CH_2)$ was ~2923–2924 cm^{-1}, demonstrating essentially no ordering of alkyl groups on the surface (Figure 3).

Convex Surfaces. If grafted molecules supported on a concave surface experienced more steric hindrance than molecules supported on a flat surface, one may anticipate the opposite for a convex surface. The results obtained supported this intuitive conclusion. The grafting density of CAMs supported on nonporous fumed silicas ($R \sim 3.5$ and 6 nm) was close to its maximum and virtually independent of the size of the alkyl for small and intermediate chains (n = 1–16) and showed a small decrease for very long chains ($n > 18$; Figure 2). We believed that the negative curvature of the substrate alleviated steric hindrance in CAMs enough so that the long-chained alkylsilanes showed the same high grafting density as trimethylsilyl groups. The CAMs showed the highest degree of molecular ordering among all of the substrates studied in this work. For the long-chained CAMs ($n > 18$), the $\nu_a(CH_2)$ frequency was ~2917–2918 cm^{-1}, indicating highly ordered alkyl surfaces comparable to the closely packed SAMs of alkyltrichlorosilanes.

Table 3. C Constants of the BET Equation for Nitrogen Adsorption on CAMs Supported on Different Silicas

	silica substrate		
grafted group in CAM	Aerosil 200	Jupiter	SBA-15
$-SiOH$ (bare silica)	100	140	200
$-Si(CH_3)_3$	12	11	15
$-Si(CH_3)_2C_4H_9$	15	18	20
$-Si(CH_3)_2C_8H_{17}$	15	20	22
$-Si(CH_3)_2C_{18}H_{37}$	18	22	27

Adsorption of Nitrogen on CAMs Supported on Concave, Convex, and Smooth Substrates. The adsorption isotherms for bare silicas and silicas with CAMs belonged to the physical adsorption type isotherms with capillary hysteresis loops (for porous samples). For all of the adsorbents studied, a good fit to the BET equation was obtained in the region of relative pressures $p/p_0 \sim$ 0.05–0.3. The intensity of the adsorption interactions of nitrogen with the surface of CAMs was assessed from the constant C of the BET equation,[25] $C \cong \exp(\Delta H_{ads}/RT)$. The C constants are given in Table 3.

Bare silicas demonstrated high values of C constants (~100–200), which were indicative of the high-energy surfaces of OH groups.[26–28] Attachment of CAMs on silica greatly reduced the energy of adsorption interactions; the C constants dropped down an order of magnitude, indicating the low-energy surfaces of alkyl groups. CAMs of trimethylsilane showed C constants close to 11–12, the value characteristic for the closely packed layer of CH_3 groups.[27–31] For CAMs of longer alkyls, C constants increased up to 20–30, which was attributed to surfaces of mixed CH_2 and CH_3 functionalities. Close inspection of the data in Table 3 showed that CAMs supported on concave surfaces demonstrated somewhat higher C constants than CAMs supported on flat and convex surfaces, respectively. We attributed this to a higher fraction of the CH_2 groups available for the adsorption for CAMs supported on concave surfaces as compared to CAMs on convex and flat surfaces, respectively. It is noted that this also could be attributed to an increase of the residual OH groups on silica. On the basis of the adsorption data, it was not possible to rule out whether the CH_2 or OH functionalities (or both) contributed to an increase of the energy of adsorption interactions. In either case, however, an increase of the C constant in the range of convex−flat−concave surfaces was consistent with an increase of the surface disorder of CAMs, corroborating the results of the grafting density and FTIR.

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Conclusion

The structure of CAMs of alkyldimethylsilanes supported on solid surfaces was determined by an interplay of two factors: (1) the length of alkyl group and (2) the curvature of the surface. Three basic types of silica substrates with different geometries were compared: concave, convex, and nearly flat surfaces. The results of chemical analysis, FTIR, and nitrogen adsorption (77 K) suggested that the concave surfaces hindered while the convex surfaces assisted the formation of closely packed and highly ordered CAMs. For CAMs of intermediate and long alkyl chains (*n* > 8), the grafting density increased (by ~20–40%), the molecular ordering improved, and the energy of adsorption interactions decreased in the following range of substrates: concave surface−flat surface−convex surface.

Acknowledgment. The authors thank Merck, Inc., for support.

Supporting Information Available: Additional information on the calculation of the grafting density using the rigid-balls model for concave and convex substrates. This material is available free of charge via the Internet at http://pubs.acs.org.

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