Adsorption Properties of SAMs Supported on TiO$_2$ and ZrO$_2$

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This work investigates vapor-phase adsorption on self-assembled monolayers (SAMs) supported on TiO$_2$ (rutile and anatase) and on ZrO$_2$ (monoclinic). Synthesis of the adsorbents was made via reactions of organosilicon hydrides (RSiH$_3$, R = C$_{18}$H$_{37}$; C$_8$H$_{17}$; C$_6$F$_{13}$(CH$_2$)$_2$; CH$_2$=CH(CH$_2$)$_6$; H$_3$Si(CH$_2$)$_8$) with metal oxide powders. The reactions yielded closely packed surfaces with high grafting densities of organic groups (up to 4.85 groups/nm^2). Adsorption properties of the materials obtained were studied by low-temperature nitrogen adsorption. All the adsorption isotherms obtained belonged to the physical adsorption isotherms (type II) and in the region of relative pressures $p/p_0 \sim 0.05-0.3$ fit the BET equation. For the modified surfaces the adsorption isotherms were substantially less convex than those for bare metal oxides, indicating a significant decrease in the energy of the adsorption interactions. According to the C constants of the BET equation, the energies of the adsorption interactions for different SAMs range as follows: C$_{18}$H$_{37}$ ≤ C$_8$H$_{17}$ ≤ C$_6$F$_{13}$(CH$_2$)$_2$ < CH$_2$=CH(CH$_2$)$_6$ ≈ H$_3$Si(CH$_2$)$_8$ ≪ bare MO$_2$. The low values of C constants observed suggested that nitrogen molecules interacted primarily with terminal groups of the closely packed SAMs and did not interact with the metal oxide substrate. C constants increased as grafting density of SAMs decreased. No substantial differences in the adsorption behavior were found for the SAMs supported on different crystalline forms of metal oxide (rutile and anatase) or on different metal oxides. Comparison of the specific surface areas before and after surface modification suggested different space requirements for nitrogen molecules adsorbed on SAMs and on bare metal oxide. The best agreement was found for a_{N_2}(SAMs) ≈ 1.2a_{N_2}(MO$_2$).

Introduction

Covalent attachment of organic molecules to the surfaces of inorganic substrates has been the focus of research and technology for a variety of applications including sorption and separation media, wetting and adhesion, fillers, pigments, sensors, biomaterials, and optical and electronic devices.[1-3] For metal oxide substrates the most powerful and widely used approach employs attachment of organosilanes (R$_{4-n}$SiX$_n$, n = 1, 2, 3) to the surface. In the case of trifunctional organosilanes, the reaction can be illustrated as follows:

(1)
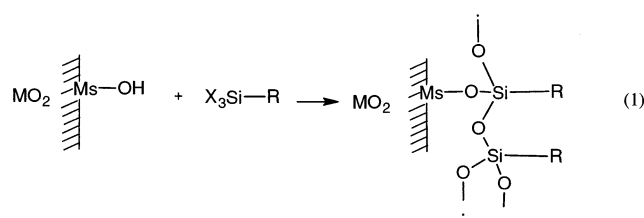
Due to formation of closely packed monolayers with relatively high ordering, this process is referred to as surface self-assembly and the monolayers prepared are called self-assembled monolayers (SAMs). Molecules in these SAMs are strongly bonded with neighbors and, to a small extent, with the surface. The best monolayers are composed of close-packed (~4.5−5 groups/nm^2), close-to-vertical chains in an extended, all-trans conformation.[4]

Recently, we described the preparation of SAMs from organosilicon hydrides (RSiH$_3$).[5,6] The use of organosilicon hydrides for surface modification is of great interest, since it produces supported monolayers in a clean reaction media, the byproduct of the reaction being hydrogen gas or water. The reactions produced closely packed, well-ordered SAMs supported on various metals and metal oxides.

The performance of surface-modified materials in separation, catalysis, sensors, and other areas is largely determined by the adsorption at SAM−liquid or SAM−vapor interfaces. In this connection the fundamental adsorption studies of covalently modified surfaces are of great importance. Vapor-phase adsorption studies are, perhaps, the most convenient approach, since it provides information about the structure of the adsorbent (the specific surface area and pore size distribution for porous materials) and about its surface chemistry (isosteric heats of adsorption, C constant of BET equation). Vapor-phase adsorption studies of the covalently modified surfaces have been the focus of the research since the late 1950s. In the pioneer work by Kiselev with coauthors[7] demonstrated that chemical substitution of the surface OH groups on silica significantly changed its adsorption properties with respect to different adsorbates. For the past decades a number of adsorption characterizations of monolayers of different oraganosilanes supported on silica,[8-14,16,17] titania,[15] and zirconia[15] have been reported. We note,

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**Table 1. Characteristics of the Adsorbents Studied and
C Constants of the BET Equation for the Adsorption of
Nitrogen at 77 K**

metal oxide	silane	%C (wt)	grafting density (groups/nm²)	BET *C* constant
TiO₂	none	<0.02		67
(anatase)	$H_3Si(CH_2)_8SiH_3$	0.43	2.75	19
	$CH_2=CH(CH_2)_6SiH_3$	0.62	3.9	19
	$C_6F_{13}(CH_2)_2SiH_3$	0.65	3.63	14
	$C_8H_{17}SiH_3$	0.59	3.81	13
	$C_{18}H_{37}SiH_3$	1.46	4.23	13
TiO₂	none	<0.02		87
(rutile)	$C_{18}H_{37}SiH_3$	6.48	4.85	13
ZrO₂	none	<0.02		75
(monoclinic)	$C_8H_{17}SiH_3$	1.23	4.5	14
	$C_6F_{13}(CH_2)_2SiH_3$	1.13	3.84	15
	$C_{18}H_{37}SiH_3$	2.56	4.43	13

however, that practically all the work has been done with the surfaces prepared from monofunctional organosilanes $(XSi(CH_3)_2R)$[8–15] or oligomeric grafted siloxanes.[16,17] Very little is known about adsorption on the surfaces of closely packed SAMs. Fundamental adsorption studies of SAMs are needed, as they provide useful information about the adsorption mechanisms and intermolecular interactions at the interfaces of well-defined chemistry.

In the present work we report the results on the vapor-phase adsorption studies of the SAMs of organosilicon hydrides with different end-functional groups supported on titanium and zirconium dioxides. The main characterization of the adsorbents is done using low-temperature nitrogen adsorption, and the results are supported by chemical analysis and FTIR.

Experimental Section

General Information. The adsorbents were prepared by the reactions of organosilicon hydrides (RSiH₃) with titanium and zirconium dioxides, as described in ref 6. According to chemical analysis, FTIR, and TGA,[6] the reaction of RSiH₃ produced closely packed, well-ordered organic monolayers supported on metal oxides (eq 1). The characteristics of bare metal oxides and of the adsorbents prepared are given in Table 1.

Adsorption isotherms were measured using the Coulter Omnisorp 100CX automated gas sorption analyzer. The apparatus was operated in the static volumetric mode for measuring all of the isotherms. Nitrogen used for both the adsorption measurements and temperature stabilization of the samples was purchased from Airgas (Piscataway, NJ). The adsorption isotherms were measured to a maximum p/p_0 of 0.50. Analysis of the adsorption isotherms was done using the BET equation:[18]

$$\frac{p/p_0}{n(1 - p/p_0)} = \frac{1}{n_m C} + \frac{(C - 1)}{n_m C}\frac{p}{p_0} \qquad (2)$$

where p/p_0 is a relative equilibrium pressure, n is an amount

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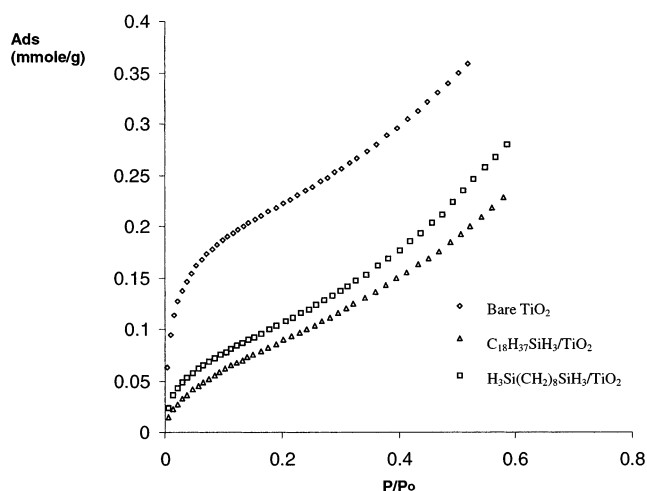
Figure 1. Nitrogen adsorption isotherms (77 K) for SAMs supported on TiO₂ (anatase).
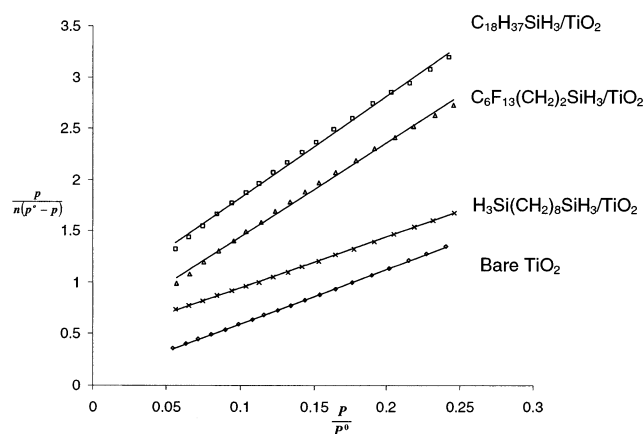
Figure 2. Adsorption isotherms in the coordinates of the BET equation.

adsorbed, and n_m is a monolayer capacity. The adsorption isotherms were plotted in the coordinates $(p/n(p_0 - p)$ versus $p/p_0)$. Correlation coefficients of the BET plots were ∼0.98−0.99 (Figure 2). The adsorption monolayer capacity (n_m) and *C* constant were determined from the slope and from the intercept of these plots.

Results and Discussion

The adsorbents were prepared via reactions of nonporous titania (rutile and anatase) and zirconia (monoclinic) powders with five organosilicon hydrides of general formula RSiH₃, where R = C_8H_{17}; $C_{18}H_{37}$; $(CH_2)_2C_6F_{13}$; $(CH_2)_6-CH=CH_2$; or $(CH_2)_8SiH_3$. Optimization of the synthesis and characterization of these materials (FTIR, TGA, and chemical analysis) has been done in our previous work.[6] As one can see from Table 1, the adsorbents prepared demonstrate a high grafting density of organic molecules, indicating formation of closely packed SAMs on the surfaces of metal oxides (eq 1). A series of nine adsorbents containing different functionalities and prepared from different metal oxides has been investigated. The main focus of the current study was to assess the role of the end-functional groups on the adsorption properties of the SAMs.

Adsorption Isotherms and Energy of Adsorption Interactions for Different SAMs. Typical adsorption isotherms obtained for bare metal oxides and for metal oxides with grafted SAMs are shown in Figure 1. According to the classification,[19] all the adsorption isotherms obtained belong to the type II isotherms, which corresponds

to a physical adsorption of N_2 on the surfaces of SAMs. Figure 2 presents linearization of the adsorption isotherms in coordinates of the BET equation.

It is noted that the isotherm for bare metal oxides is substantially more convex than those for SAMs (Figure 1). This can be explained as weakening of the adsorption interactions and is consistent with the hydrophobic nature of the SAMs. Similar observations have been made in previous publications on the adsorption characterization of different organic monolayers supported on metal oxides.[7–17,24] The intensity of the adsorption interactions with SAMs can be assessed from the constant C of the BET equation (eq 2). The C constant is related to the heat of adsorption[18,19] and can be expressed as follows:

$$C = \frac{a_1 b_2}{a_2 b_1} \exp\left(\frac{q_1 - q_{\mathrm{L}}}{RT}\right) \qquad (3)$$

where a_1, a_2, b_1, and b_2 are constants connected with the formation and evaporation of the first and the second (and higher) layers of an adsorbate. q_1 is the heat of formation of the first adsorbed layer, q_{L} is the heat of condensation of an adsorbate, and $q_1 - q_{\mathrm{L}} = \Delta H$ is a reduced (pure) heat of adsorption. R is the gas constant, and T is the absolute temperature. According to the authors of the BET model,[18] the factor $a_1 b_2 / a_2 b_1$ is close to unity and an average heat of adsorption can be estimated as follows:

$$\Delta H \cong RT \ln C \qquad (4)$$

However, there is a notable inconsistency in the literature, and several groups have suggested alternative assumptions about the pre-exponential factor in eq 3. It has been pointed out that this factor can be smaller[20,21] and greater[22] than unity. The authors[23] demonstrated that the value of this factor depends on the entropy of adsorption and is equal to unity when the entropy of adsorption is equal to the entropy of liquefaction of an adsorbate. General analysis of this issue is beyond the scope of the present publication, and in this work we are assuming that the factor $a_1 b_2 / a_2 b_1$ is constant for the adsorption of nitrogen on different SAMs. With this assumption we will use C constants as an estimate for the energy of the adsorption interactions.

C constants for the adsorbents studied in this work are given in Table 1. Nonmodified (bare) titania and zirconia demonstrate high values of C constants ($\sim 70-90$), which is consistent with the high energy surfaces of hydrated metal oxides (surface OH groups) and agrees well with the data reported in the literature.[7–10,19] As one can see from Table 1, C constants for all SAMs are notably smaller than those for the bare oxides and range between 13 and 19. According to the C constants, the following range of the energy of the adsorption interactions with different SAMs was established:

$$C_{18}H_{37} \approx C_8H_{17} \leq C_6F_{13}(CH_2)_2 < CH_2{=}CH(CH_2)_6 \approx$$
$$H_3Si(CH_2)_8 \ll \text{bare MO}_2$$
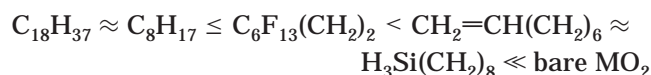
We note that no substantial differences in the adsorption

isotherms and C constants were found for SAMs supported on TiO_2 (rutile and anatase) and on ZrO_2 (monoclinic).

On the basis of the results obtained above, some speculations about the mechanism of the adsorption on the SAMs can be made. Low values of C constants observed for $C_{18}H_{37}$ and C_8H_{17} SAMs ($C \sim 13-14$) suggest that adsorption takes place primarily on alkyl groups and not on the metal oxide. Closely packed alkyl chains of the SAMs effectively shield the polar surface of the metal oxide (residual OH groups), acting as a structural barrier that prevents nitrogen molecules from interacting with the substrate. According to the literature, the BET C constant for the adsorption of nitrogen on the surface of methyl (CH_3) groups is $11-12$. These numbers have been reported for closely packed monolayers of trimethylsilane ($C = 11$[25] and $C = 12$[9]) and oligo-(dimethylsiloxane)[16] ($C = 12$) supported on silica. Surfaces that contained accessible methylene groups (CH_2) possess somewhat higher surface energy[26] and demonstrate slightly higher values of the C constant than methyl-terminated surfaces. For example, monolayers of long chained alkyldimethylsilane that contained disordered alkyl chains and expose substantial amounts of CH_2 groups on the surfaces show C constants around 20.[16,25] In the forthcoming publication[25] we are proposing that the values of the C constant of the BET equation can be used for the accurate characterization of the surface energy of the hydrophobic monolayers. In this paper we are limiting ourselves to the following statement: C constants of $13-14$ obtained for closely packed SAMs of alkylsilanes suggest that nitrogen molecules interact primarily with the surface of methyl and methylene groups and not with the surface of metal oxide. As will be shown later, the presence of accessible OH groups on the surface (e.g. for incomplete SAMs) results in a notable increase of the C constant.

SAMs prepared from 7-octenyl- and 1,8-bis(hydridosilyl)octylsilane demonstrate C constants of 19, which is consistent with the case for surfaces that consist of methylene and vinyl groups. SAMs of C_6F_{13} deserve a special comment. Surfaces of closely packed fluoroalkyl groups have the lowest possible surface energy[26] and, in principle, should have the lowest energy of adsorption interactions. However, C constants obtained for C_6F_{13} SAMs were $\sim 14-15$. We explain this as due to additional specific interactions between nitrogen quadrupoles and C–F dipoles. The C constant for the nitrogen adsorption on Teflon[27] is 20, which supports this assumption. Alternatively, a relatively high value of the C constant for fluoroalkyl SAMs can be explained as penetration of nitrogen molecules in the monolayer and interaction with the OH groups of the metal oxide. We note, however, that this would result in an increase of the specific surface area for the adsorbents with SAMs, which disagrees with the experiments (see Table 2 and the next section).

By preparing SAMs with incomplete surface coverage, one can control the energy of adsorption interactions over a wide range. As is shown in Figure 3, C constants and, therefore, heat of adsorption increase as the grafting density of SAMs is decreased. This trend is consistent with an increase of the polar adsorption centers (residual OH groups on the surface of metal oxide) available for the interactions with an adsorbate on the surfaces of incomplete SAMs.

Space Requirements for the Adsorption of Nitrogen on SAMs and Surface Area of the Adsorbents.

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Table 2. BET Surface Area and N₂ Cross-Sectional Area for the Adsorption on SAMs

adsorbent	S_{BET}^{a} (m²/g) using a_{N_2} = 13.5 Å²	a_{N_2}(SAM)[b]
TiO₂ (anatase)	10	
(TiO₂)−Si(CH₂)₈SiH₃	8	16.9
(TiO₂)−Si(CH₂)₆CH=CH₂	8.5	15.9
(TiO₂)−Si(CH₂)₂C₆F₁₃	8.4	16.1
(TiO₂)−SiC₁₈H₃₇	8	16.9
ZrO₂ (monoclinic)	17.5	
(ZrO₂)−SiC₈H₁₇	16	14.8
(ZrO₂)−Si(CH₂)₂C₆F₁₃	13	18.2
average		16.5 ± 1.5

[a] Surface areas of modified metal oxides are calculated per gram of metal oxide. [b] = $S_{BET}(MO_2)/S_{BET}(SAM) \times 13.5$ (Å²).

The BET surface areas of the adsorbents studied are given in Table 2. The data of Table 2 show that the surface areas of the adsorbents with SAMs undergo a substantial decrease (∼20% on average) as compared to those of bare metal oxides. BET surface area is calculated from the monolayer's capacity (n_m, eq 2) as follows:

$$S_{BET} = n_m a_{N_2} N_A$$

N_A is Avogadro's number and a_{N_2} is the cross-sectional area of the nitrogen molecule in the adsorbed state. If particles of an adsorbent are nonporous, SAMs are uniform, and their thickness is small compared to the particle size (see the comment below), a decrease in the surface area must be related to an increase in a_{N_2}. For bare metal oxides we used a_{N_2} = 13.5 Å², the value recommended by Jelinek and Kovats.[10] To have the surface areas for the adsorbents with SAMs equal to those of bare metal oxides, one should use the corrected values of a_{N_2} that are shown in the last column of Table 2. As one can see, these values scatter between 14.8 and 18.2 Å² with an average value of a_{N_2} = 16.5 ± 1.5 Å². This result is in excellent agreement with 16.2−17.5 Å², the numbers given in work[10] for the adsorption of nitrogen on hydrophobic monolayers supported on silica. Increase (by ∼20−30%) of the cross-sectional area has also been reported[9,27,28] for the adsorption of nitrogen on dehydrated silica (hydrophobic) versus hydrated silica (hydrophilic).

It is noted that careful analysis of the surface area requires accounting for the change in the specific surface area due to an increase in the particle diameter after modification with SAMs. The calculations, however, show that these changes are rather small and, in the first approximation, can be ignored. The average particle diameter of bare metal oxides can be found from density and BET surface area (assuming spherical shape of particles). Calculation gives 160 nm for TiO₂ anatase and 60 nm for ZrO₂. The increase in the BET surface area due

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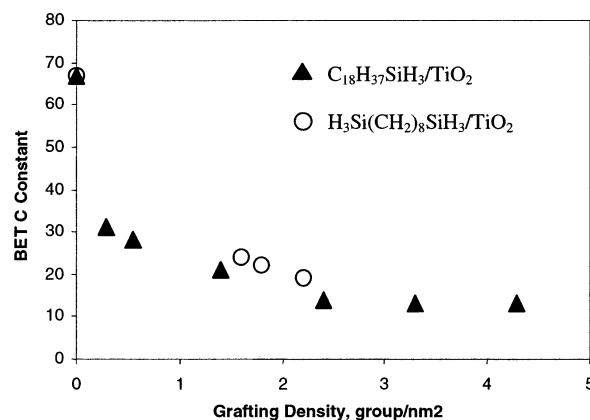
Figure 3. Effect of grafting density on the *C* constant of the BET equation for the adsorption on incomplete monolayers on TiO₂ (anatase).

to the SAM can be calculated as follows: $S_{SAM}/S_{MO_2} = ((D_0 + 2h)/D_0)^2$, where S_{SAM} and S_{MO_2} are the surface areas of the MO₂-SAM and bare MO₂ expressed in square meters per gram of MO₂. D_0 is an average diameter of particles of bare metal oxide, and h is the thickness of the SAM. For octadecyl-SAMs we used h = 2.5 nm, and for octyl-, octenyl-, 1,8-bis(hydrosilyl)octane-, and tridecafluorooctyl-SAMs h = 1.2 nm. It was obtained that surface area increases by ∼3−6% for TiO₂-SAMs and by ∼8% for ZrO₂-SAMs. Thus, the a_{N_2} values in the last column of Table 3 should be decreased by 3−8%, respectively. The exact analysis of this issue, however, would require discussion of particle shape and morphology and is beyond the scope of this paper.

In conclusion, the adsorption properties of closely packed SAMs of RSiH₃ supported on titanium and zirconium dioxides have been characterized. SAMs provide good shielding of the surface of metal oxides. The energy of adsorption interactions (assessed from the *C* constant of the BET equation) was determined by the end-functional group (R) of the SAM and by its grafting density and not by the metal oxide. No substantial differences in the adsorption behavior were found for the SAMs supported on different crystalline forms of metal oxide (rutile and anatase) or on different metal oxides. Surface area measurements suggested different space requirements (∼20% increase in the a_{N_2}) for the adsorption on SAMs versus adsorption on bare MO₂.