Direct Diffusion Measurements of Naphthacene on Silica as a Function of Silanol Density[1]

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Abstract: Fluorescence photobleaching is employed to obtain directly, and for the first time, diffusion coefficients and mobile fractions for naphthacene adsorbed on silica gel. The diffusion is slower than that estimated from bimolecular rate constants in comparable systems, and only about one-third to one-half of the molecules are mobile. The mobility parameters are studied as a function of the level of hydroxylation (chemisorbed water) and hydration (physisorbed water) of the silica gel controlled by appropriate heat treatments. The diffusion coefficient is independent of the preparation while the mobile fraction increases when the level of hydroxylation decreases and that of hydration is increased. These trends are rationalized in terms of the surface heterogeneity and the number of hydrogen bonds formed between naphthacene and surface silanol groups.

Surface diffusion is presumed to occur during catalysis, photochemical reactions, and photophysical processes in heterogeneous media.[2-12] The vast majority of surface diffusion studies have measured movement of a gas or a metal as the adsorbate on metal surfaces under conditions where these species are chemisorbed, i.e. bound to the surface with energies on the order of a hundred kilojoules per mole or more.[13-16]

Surface diffusion on metal oxides (silica, alumina) is less studied because of the lack of suitable tools for making direct measurements of diffusion rather than for a lack of interest. Photochemical and photophysical kinetic studies of adsorbed polyaromatic hydrocarbons (PAH)[3-10] have provided indirect evidence for surface diffusion, and in a few cases the mobility has been estimated through second-order rate constants for bimolecular processes.[7,9,12] The interactions between the surface and adsorbate in these systems are characterized by physisorption, which occurs by a bonding between surface hydroxyl groups and the π electron system of the polyaromatic hydrocarbon[17,18] and is on the order of tens of kilojoules per mole.[5,13]

We have become interested in understanding how multiple weak interactions between an adsorbate and a surface will affect the mobility of the adsorbate. Will, for example, the presence of four or more physisorption sites per molecule render it immobile? To address this question we have started direct measurements of diffusion of long polyaromatics (naphthacene[19] and pentacene) on silica surfaces with various degrees of hydroxylation.

We report here on the first application of fluorescence photobleaching techniques to measurements of diffusion of aromatic adsorbates on silica. We find that the diffusion rate of naphthacene is independent of the extent to which the surface is hydroxylated or hydrated but that the fraction of molecules that are free to diffuse micrometer distances varies by a factor of 2 depending on the number of hydroxyl groups per unit area of the surface. These results are discussed in the context of the ease of adsorption, the heterogeneity of the surface distribution, and the number of adsorption sites per molecule.

Experimental Section

Sample Preparation. Naphthacene (Aldrich) was recrystallized from benzene prior to use. Concentrations of degassed naphthacene solutions (obtained by bubbling with nitrogen or freeze–pump–thaw cycling) in spectroscopic grade cyclohexane were determined by absorption spectroscopy (ϵ = 14 000 M^{-1} cm^{-1}, λ = 471 nm[20]).

For all samples the silica gel (Mallinckrodt, surface area 300 m^2 g^{-1}, average pore diameter 150 Å) was kept in an 180 °C oven for at least 1 week prior to use. The silica was then cooled in a desiccated chamber to room temperature. Once cooled, the silica was put into a vacuum chamber and heated under vacuum for a period of not less than 4 hours. This pretreatment temperature ranged from room temperature (25 °C) to 600 °C. The silica was cooled to room temperature prior to addition of a naphthacene solution to the vacuum chamber.

Deposition of the adsorbate was achieved by either sublimation or direct solvent evaporation. Sublimation is achieved by adding naphthacene solution to a compartment other than the one occupied by the silica. The solvent is removed slowly by evaporation. The solid naphthacene formed and the silica are mixed and agitated for about 30 s. In this time most, if not all, of the naphthacene will sublime onto the silica. Samples are left on the vacuum line for another hour to approach equilibration. Deposition from solution is just that, mixing the solution and the silica and removing the solvent slowly.

Sublimation provides a way of adding the adsorbate without other alterations of the surface composition, while deposition from cyclohexane invariably leads to addition of trace amounts of water. This was used to add, reproducibly, water to the extent of about 0.2 μmol m^{-2} (2% of a monolayer).

The samples are sealed by a stopcock and maintained evacuated while mounted on the microscope stage for diffusion measurements.

All samples were prepared to have a surface coverage of naphthacene to be 8×10^{-3} μmol m^{-2} or roughly 0.1%. This assumes a surface area of 60 $Å^2$ per molecule of naphthacene,[21] which does not account for the van der Waals radii of interaction. If we account for these the surface coverage is 0.3%.

All measurements are made at room temperature with the sample held in a quartz cuvette with a 1 mm path length.

Fluorescence Photobleaching. Measurement of diffusion and mobile fractions by fluorescence photobleaching is a well-established technique in membrane biology and has been applied successfully for more than a decade in a number of biological contexts.[22,23] The approach has also

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been used to measure diffusion of substrates on monolayers of lipids at water–air interfaces and at monolayers of lipids attached to solids.[24-26] We believe the present experiments represent one of the first attempts at applying this technique to measure the diffusion of small molecules directly on a solid substrate.

Fluorescence photobleaching experiments entail generating concentration gradients in the fluorescent molecules by a rapid photolysis and subsequently observing the relaxation of the imposed gradients by diffusion. From the rate and extent of fluorescence recovery the diffusion coefficient, D, and the mobile fraction, X_m, can be determined.[27,28] A Coherent 4 W continuous wave Argon ion laser is used as the illumination source. The laser output is set to 100 mW at 476.5 nm and is further attenuated by optics and neutral density filters such that the laser power of a weak beam, used to monitor the fluorescence intensity of the sample, is on the order of 1 μW, whereas that of a more intense beam, used to photolyze a part of the sample, is a few milliwatts at the sample. The duration of the bleach pulse is 150 ms. The total monitor time is approximately 51 s (512 channels at 100 ms/channel).

The Gaussian laser beam is focused by using a 140 mm lens and a 40 power microscope objective to a waist radius at the sample of 1.1 μm. (**Note Added in Proof**: The beam is focused at the top surface of a single silica bead and the emission is detected principally from this surface. Even though the laser beam will penetrate further into the bead where light scattering will arise, the majority of fluorescence from this region is eliminated by an image plane pin hole. Artifacts from light scattering within a silica bead should be minor.) Fluorescence emission is monitored through a Zeiss Universal epifluorescence microscope as described previously.[28]

Data acquisition and storage is accomplished by use of a Digital MINC computer, which also controls the electronic components. The parameters D and X_m are extracted by a complete fit to the series solution for the diffusion recovery given the Gaussian laser beam geometry.[27] Analysis of the data is performed on a VAX6330 with methods described previously.[28]

If the sample contains a single mobile species, the diffusion coefficient is representative of that species, and the mobile fraction measures the fraction of that species which is free to move within the time scale of the experiment.

If there is more than one mobile species, the recovery represents a complex superposition of several recovery curves, and a molecular interpretation of the measured diffusion is difficult. In this case, the mobile fraction represents the proportion of all species that are mobile.

In the special case where a single molecular entity (here naphthacene) may sample a number of different environments the recovery is a measure of the weighted diffusion coefficient for each of the dynamically interchanging environments

$$D = \sum_i f_i D_i \qquad (1)$$

where f_i represents the fraction of time the molecule resides in a particular environment in which the diffusion coefficient is D_i. This is equivalent to weighting by the relative amounts of naphthacene in each environment at any particular time.[29,30] In this situation, the mobile fraction measures the proportion of the molecules that exchange among the mobile environments in contrast to those that reside permanently in fixed sites.

Results

Quantitative Observations. A typical example of a photobleaching diffusion measurement is shown in Figure 1 along with the fit to the recovery. In the evacuated samples, where there is no oxygen present, the photolysis reaction leads to the formation of naphthacene dimers[31-33] that may or may not be mobile.

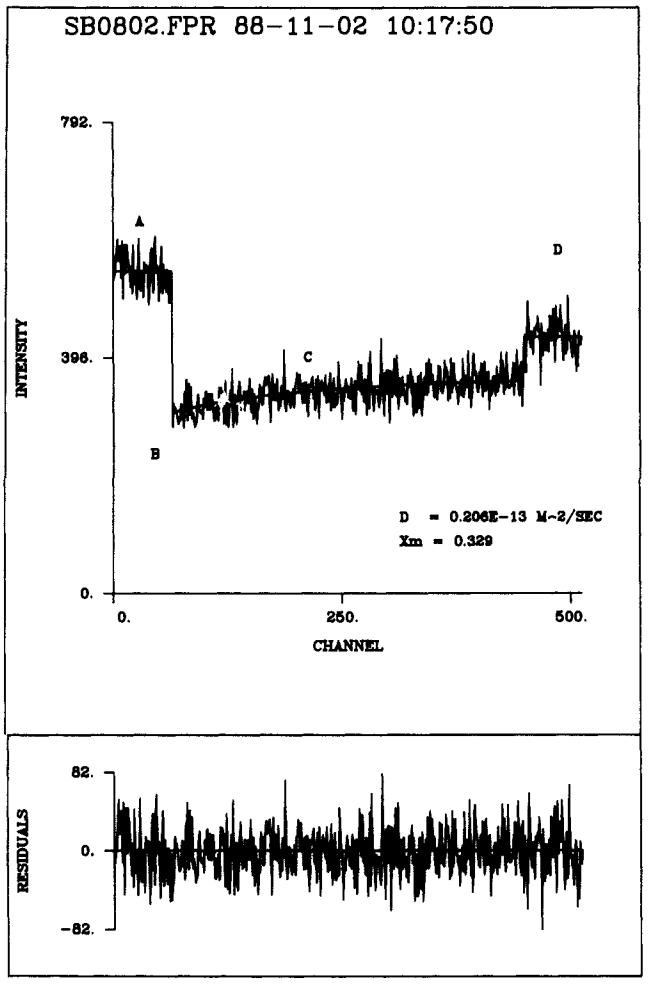

Figure 1. Typical plot of FPR data: region A, initial fluorescence intensity; region B, immediately after the bleach pulse; region C, the recovery of the fluorescence intensity; region D, fluorescence intensity after very long time. This plot is for a sample of 0.1% coverage naphthacene adsorbed on dry silica. Experimental details: 100 ms/channel, 512 channels, 150 ms bleach pulse, a 50 s post-recovery pause following region C. No laser light reaches the sample during this period.

Table I. Diffusion Coefficients and Mobile Fractions of Naphthacene on Dry and Hydrated Silica as a Function of Pretreatment Temperature

(A) Diffusion Coefficients

	dry		hydrated	
T_p, °C	D, 10^{-14} m^2 s^{-1}	N[a]	D, 10^{-14} m^2 s^{-1}	N
25	2.3 ± 0.4[b]	103	2.8 ± 0.4	107
250	2.6 ± 0.5	78	1.8 ± 0.2	92
400			2.6 ± 0.4	98
600	2.2 ± 0.5	42	3.2 ± 0.4	83

(B) Mobile Fractions

	dry		hydrated	
T_p, °C	X_m	N	X_m	N
25	0.37 ± 0.04	103	0.51 ± 0.03	107
250	0.33 ± 0.04	78	0.50 ± 0.03	92
400			0.55 ± 0.04	98
600	0.53 ± 0.07	42	0.67 ± 0.03	83

[a] N is the number of experiments. [b] Errors reported as SEM at a 97.5% confidence level.

Recovery of the fluorescence intensity can arise from reversible photochemistry, but in the present case the dimers formed are known to be stable in the absence of ultraviolet radiation.[31]

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Rotational diffusion can contribute to the recovery if the polarized excitations selectively monitor and photobleach molecules with particular orientations. This process usually leads to complete recovery of fluorescence but cannot be totally excluded from the present system. The rate of recovery is more suggestive of a translational diffusion process and is then due to diffusion of naphthacene which has never been exposed to light, from regions surrounding the 4 μm^2 area in which the photolysis occurs. The rate of diffusion of naphthacene should be unaffected by the presence of the dimers since the overall surface coverage is very low (0.1–0.3%). Each diffusion measurement can be made with a precision of 10–20% depending on the extent of recovery, but to improve the accuracy it is necessary to perform a large number of measurements on a given sample.

Table I shows diffusion data for naphthacene adsorbed on dry silica gel and silica gel with 2% water coverage as a function of the pretreatment temperature (T_p). It is evident that the diffusion coefficient (Table IA) is insensitive to the surface treatment and remains at a constant value of $(2.4 \pm 0.2) \times 10^{-14}$ m^2 s^{-1} for all the dry silica samples and at $(2.5 \pm 0.7) \times 10^{-14}$ m^2 s^{-1} for the sample with added water. Adsorption of approximately a monolayer of myristic acid to the silica gel prior to addition of naphthacene resulted in samples in which the naphthacene diffusion was 10-fold faster ($D = 2.6 \times 10^{-13}$ m^2 s^{-1}). The diffusion coefficient is therefore insensitive to the extent of surface hydroxylation or hydration, but it is sensitive to whether the naphthacene is bound to a silica surface or a hydrophobic surface provided by the physisorbed myristic acid.

Table IB shows the mobile fraction of naphthacene on each of the samples for which the diffusion coefficient was found to be invariant. For both dry and slightly hydrated surfaces, the mobile fraction increases significantly as the pretreatment temperature is raised. For equivalent T_p values, the mobile fraction is consistently greater for the slightly hydrated samples. The largest mobile fraction observed in any of the samples was that of 0.75 observed for the myristic acid sample. It should be noted that a mobile fraction between 0.3 and 0.7 represents a significant degree of mobility, and the measurements in this range are generally very reliable.

The data presented in Table I are averages obtained from 42 to 107 individual diffusion measurements on at least four separately prepared samples of each type. Among the samples the results are consistent. Nevertheless, there is a sizable variation in the data as illustrated in Figure 2 for the diffusion coefficients and mobile fractions for the dry samples. These histograms show the substantial shift in the distribution of mobile fractions at the high temperature. At this point we attribute the width of the distribution to heterogeneity in the surface coverage and contour.

Qualitative Observations. The heterogeneity of naphthacene coverage on the surface of the silica gel is implicit in the variation in diffusion coefficients and mobile fractions observed within the same sample. Further evidence is seen by the relative number of microcrystals of naphthacene discernible in the fluorescence microscope. Although the numbers were not quantified, it was clear that their occurrence was more frequent in samples dehydroxylated at high pretreatment temperatures. The most frequent occurrence of microcrystals was observed in a sample excessively hydrated at the 10% level. In this case, the fluorescence distribution in regions without microcrystals was so low as to make measurements very difficult, and frequently meaningless. In the myristic acid coated samples there was no evidence of microcrystals forming.

A corollary to excessive formation of microcrystalline domains is that the number of successful diffusion measurements decreases. This is because in regions with large density of microcrystals, the fluorescence is predominantly from these solids. Since the microcrystals are immobile, the photobleaching experiments show so little recovery that it is impossible to get a reliable measure of the diffusion coefficient. In line with the qualitative observations outlined in the previous paragraph, we also observed that for samples pretreated at room temperature, the success rate was almost unity while at the higher T_p's the success rate was less than half. Generally, the success rate was greater in the slightly hydrated samples.

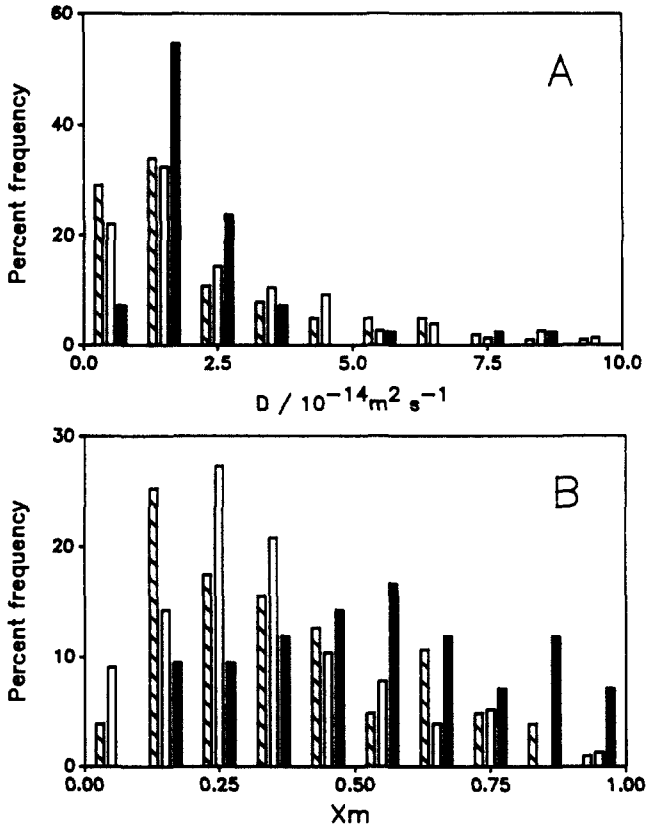

Figure 2. Frequency of occurrence of diffusion coefficients (A) and mobile fractions (B) within intervals representing 10% of their range. These histograms show distributions of D and X_m for naphthacene adsorbed on dry silica at various pretreatment temperatures (25 °C diagonal, 250 °C blank, 600 °C solid).

For all the dry samples, irrespective of the pretreatment temperature, the rate of sublimation *onto* the silica gel was comparable. However, if the samples are left on the vacuum line for extended periods of time, there is a slow desorption which is observed as a coloration of a cotton plug positioned between the sample and the sample chamber exit port. This rate of desorption is sensitive to the silica treatment. There is virtually no desorption from the room temperature treated samples, whereas significant desorption occurs from samples treated at 600 °C occurs over a period of a few hours from samples treated at 600 °C.

These qualitative observations point toward the same trend: samples treated at low temperatures adsorb the naphthacene more strongly, therefore competing more effectively for the naphthacene, minimizing the tendency for naphthacene crystal to form, and inhibiting the desorption from the surface.

Extents of Hydroxylation and Hydration. Previous measurements on silica gel of the same type as that used here, using virtually identical treatment protocols, have revealed that the density of silanol groups decreases dramatically as the surface is heated.[33] As a consequence, the number of hydroxyl groups available to bind to a single naphthacene also decreases. Specifically, silica preheated at 25, 250, 400, and 600 °C contains 5, 4.2, 2.2, and 1.6 silanol groups per square nanometer,[34] which would allow for an average of 3, 2.4, 1.3, and 1 silanol groups per naphthacene molecule in a monolayer of naphthacene. In order to assess how most of the naphthacene might interact with the surface we estimated from these data the fraction of naphthacene molecules that could in principle interact with only a single silanol group, with only two silanol groups, with exactly three silanol groups, and with exactly four silanol groups. The calculation was purely geometrical and was based on the silanol groups distributing

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Table II. Predicted Mole Fractions of Naphthacene Bound to Exactly Two (X_2), Three (X_3), or Four (X_4) Silanol Groups as a Function of the Probability (p) that a Silicon Site Has a Single Silanol or a Geminal Pair of Silanol Groups

T, °C	p	X_2	X_3	X_4
	Single Silanols Only			
25	1.00	0.00	0.00	1.00
250	0.84	0.00	0.00	1.00
400	0.44	0.01	0.31	0.67
600	0.32	0.04	0.49	0.47
	Geminal Silanols Only			
25	0.50	0.00	0.24	0.76
250	0.42	0.01	0.34	0.64
400	0.22	0.10	0.60	0.30
600	0.16	0.20	0.60	0.20

themselves on a hexagonal lattice with a separation of 5 Å in a random pattern determined by the total density. The number of configurations that permitted exactly 1, 2, 3, or 4 silanol groups to interact with the aromatic rings of naphthacene were then counted and normalized. The results, assuming that none of the silanol groups are geminal and that all the hydroxyl functions are accessible for interaction, are shown in Table II. In all cases, the number of molecules that are bound to a single silanol group is vanishingly small at all levels of hydroxylation. In fact, one would expect the majority of the naphthacene to be bound to four silanol groups in this model. Only at the densities corresponding to pretreatment temperatures of 600 °C is there a substantial fraction of naphthacene molecules bound to exactly three silanol groups.

Water will bind to both isolated silanol groups[35] as well as silanol groups that are already hydrogen bonded.[17] Addition of water to the isolated groups will decrease the binding ability of these groups toward naphthacene.[17] The net effect is to reduce the density of silanol groups on the surface that may bind with naphthacene. A similar effect occurs if there are a large number of geminal silanol groups, or if there is a significant amount of hydrogen bonding within the surface among vicinal silanol groups. Table II also illustrates the effect on the surface distribution among the various binding environments for the case where the effective densities have been reduced by a factor of 2 to simulate the case where all the silanol are present as geminal pairs. Hence, the values in Table II represent the two extreme limits on the population distributions of naphthacene with various numbers of silanol group interactions.

Discussion

The data presented here demonstrate that as the number of silanol groups on the surface of the silica decreases, the strength of the interaction of naphthacene with the surface decreases. This is seen qualitatively as an increased ease of desorption from the surface and an increase in the number of microcrystals formed on the surface. The latter would not exist if the naphthacene surface interactions were much stronger than those between naphthacene molecules within the solid. The quantitative ramification of the decrease in the strength of interaction is a significant increase in the fraction of molecules that are free to move on the surface. The mobile fraction increases by at least 50% in the dry samples upon pretreatment at high temperatures and is even higher in these samples when they also are slightly hydrated.

Surprisingly, the rate of mobility is unaffected by the number of silanol groups in the surface since the diffusion coefficient remains essentially the same in all samples. The value is not an artifact of the technique, the probe, or the sample configuration, since identical experiments with silica coated with myristic acid clearly yield different diffusion measurements. Moreover, the naphthacene concentration on the surface is sufficiently low that the diffusion is not that of naphthacene on naphthacene. The diffusion coefficient of 2.5×10^{-14} m^2 s^{-1} is therefore real and representative of the naphthacene interactions with the silica surface.

To our knowledge, there are no other direct measurements of diffusion of polyaromatic hydrocarbons on solid surfaces. For comparison naphthacene diffuses at a rate of 1.1×10^{-11} m^2 s^{-1} in fluid lipid membranes,[36] about 500-fold faster than on silica, and 50 times the rate measured on myristic acid coated silica.

Diffusion of tetraethyllead on sapphire was previously estimated by photochemical desorption rate measurements to be about 3×10^{-11} m^2 s^{-1},[37] which is about three orders of magnitude faster than naphthacene on silica measured here. Presumably this difference is attributable to multiple stronger adsorbate–surface interactions in the latter case.

The diffusion of oxygen on a tungsten(110) surface has been estimated to range from 10^{-10} to 10^{-12} m^2 s^{-1},[14] depending on the surface coverage, while those for nickel on platinum are found to range from 10^{-20} to 10^{-30} m^2 s^{-1},[12] at room temperature. These numbers illustrate the enormous variation in mobility for chemisorbed species.

Excimer formation and bimolecular quenching studies have provided estimates of the bimolecular rate constants (k_2) in a number of aromatic systems adsorbed on metal oxide surfaces. The values range from 7×10^{12} m^2 mol^{-1} s^{-1} for pyrene[7] to 8×10^{11} m^2 mol^{-1} s^{-1} for acridine[9] on dry silica. Acridine was found to be immobile on alumina.[9] It is interesting to note that de Mayo and co-workers[7] have found k_2 to increase by an order of magnitude for pyrene on wet (at least a monolayer coverage) silica over that on dry silica. These differences are attributed to the bonding strength of pyrene to the different surfaces. After heating to 700 °C only isolated silanol groups are left, to which aromatic hydrocarbons will bind strongly. By covering the silica with water these binding sites are effectively blocked, and the hydrocarbon cannot bind as strongly. This allows for an increase in the mobility of adsorbed species.[7] This effect is reflected in the increase in X_m between the wet (0.2 μmol m^{-2}) and dry silica in this study.

Comparisons of these rate constants with diffusion coefficients depends on the diffusion model employed and are fraught with danger. Nevertheless, a simple-minded extension of the analysis frequently used in membrane work[8] would suggest that the above probes have diffusion coefficients on the order of magnitude of 10^{-10}–10^{-12} m^2 s^{-1}. These are somewhat faster than the direct measurements presented here for naphthacene. The origin of this discrepancy is unclear. It may be a reflection either of the inadequacy of the diffusion model to account for the fact that bimolecular interactions may occur over small distances, while the photobleaching diffusion measurements require transport over micrometer distances, or of true differences in mobility. Unfortunately the bimolecular rate constant for interaction of naphthacene with naphthacene has not been measured.

It is possible that the measured diffusion coefficient is a weighted average resulting from naphthacene interchanging rapidly among several mobile environments (eq 1). For example, if there are two environments in which the diffusion coefficient differed by a factor of 10, then the measured diffusion coefficient would change by a factor of about 2 if the time spent in the more mobile environment changes by a factor of 2. The variations in the measured diffusion coefficients with changing dehydroxylation are too small compared with experimental uncertainties to allow for a detailed analysis of this situation. The data do, however, not exclude the possibility that there exists a more mobile species which is the one primarily detected in photophysical and photochemical experiments.

Phenomenologically, the observations that the mobile fraction but not the diffusion coefficient changes in a sample is evidence that the diffusing probe exists in at least two environments, a mobile one and an immobile one, and that the exchange between the environments is slow relative to the time scale of the experiment (minutes).[30] In addition, the decrease in silanol density results

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specifically in a shift in the population of naphthacene from the immobile environment to the mobile one.

The measured mobile fraction could be affected by the exact surface topography. If the silica gel contains crevices in which the naphthacene is trapped, then these molecules would appear as immobile populations. However, the pretreatment temperatures used in this work are not expected to cause significant changes in the surface topography, other than to increase the number of siloxane bridges and decrease the number of silanol groups. Temperatures of 1000 °C or greater are required to cause irreversible surface changes.[38,39] While the surface topography variations from bead to bead may be partly responsible for the relatively large variation in the mobility measurements, they are unlikely to be the cause of the *systematic* changes in mobile fraction observed when the silanol density changes.

The presence of microscopic crystals on the surface will contribute to the immobile fraction. Our qualitative observations indicate that there are more crystalline domains present on the surface when the silanol density decreases, which should lead to decreases in the mobile fraction under these circumstances. This is precisely the opposite effect to that observed in the measurements. We must, therefore, look to the specific interaction between naphthacene and the silanol groups for an explanation of the changes in mobile fractions.

There is ample evidence that the preferred mode of interaction between polyaromatic hydrocarbons, without functional groups, and the surface of silica or alumina is via a hydrogen bond between the hydrogen in a silanol group and the π-electrons of the aromatic ring.[7,15,16] It is believed that the interaction between the aromatic ring is strongest in isolated silanol groups in part because the affinity of the aromatic ring for the hydroxyl groups involved in hydrogen bonding, either to other silanols or to water, is much weaker.[16]

Naphthacene contains four linearly arranged aromatic rings and has the potential of binding to up to four different silanol groups, presuming that naphthacene is binding to a flat surface. On a convoluted surface, there is a possibility that OH groups may bind to the same aromatic ring from both sides, but the second interaction is likely to be weaker than the first. We do not consider the effects of these additional interactions, but restrict our attention to the four possible binding environments: singly bound naphthacene (N-HOSi); doubly bound naphthacene (N-$[HOSi]_2$); triply bound naphthacene (N-$[HOSi]_3$), and quadruply bound naphthacene (N-$[HOSi]_4$).

As a first approximation, one would expect the affinity constant for the binding to the surface to increase as the power of the number of naphthacene–silanol interactions, or more precisely the enthalpy of interaction for N-[HOSi] should be only a quarter of that for N-$[HOSi]_4$. Entropy contributions are expected to be small.[40] One might expect the N-[HOSi] species to desorb more readily than either N-$[HOSi]_2$, N-$[HOSi]_3$, or N-$[HOSi]_4$.

Surface diffusion could in principle occur by either of two simple-minded mechanisms: desorption followed by adsorption, i.e. hopping along the surface, or sliding along the surface by alternating breaking of one of several naphthacene–silanol interactions and reforming another one. The only way the N-[HOSi] species can move on the surface is by a desorption–adsorption mechanism. The N-$[HOSi]_2$ species is less likely to completely desorb, but breaking one interaction would permit rotation of the naphthacene around the other, prior to formation of a new surface bond. The net effect could be a translation of the center of mass. The N-$[HOSi]_3$ species could slide across the surface by continual breaking and remaking bonds, but the probability that there are significant translational movements when only one of the three interactions is broken is smaller because of the geometric constraints of the remaining two bonds. Hence, one would expect the rate of lateral movement to be less in this environment. By analogy, the N-$[HOSi]_4$ species should be the least mobile of all the species.

An initial assessment of the surface density of silanol groups suggests that the great majority of naphthacene should exist as the N-$[HOSi]_4$ species, especially for silica treated at lower temperatures. The significant fraction of mobile molecules (>30%) indicates that this initial assessment is invalid. We would suggest that the true density of silanol groups able to bind to naphthacene is somewhat lower than that indicated in Table II because a majority of them are in fact involved in hydrogen bonding within the surface and because there is a significant fraction that exist as geminal pairs.

It is important to note that while the relative populations of N-$[HOSi]_4$ and N-$[HOSi]_3$ vary significantly with the silanol density within this range, the relative populations of N-[HOSi] and N-$[HOSi]_2$ vary little (from 0 to 4% for the N-$[HOSi]_2$ population).

The data presented here are consistent with the proposal that the N-$[HOSi]_4$ and N-$[HOSi]_3$ species are the dominant species; that the N-$[HOSi]_4$ species is immobile on the time scale of the measurement while N-$[HOSi]_3$ is the principal species being observed moving; that the N-$[HOSi]_2$ and N-[HOSi] populations are so small as to not affect the experiment; and that the change in silanol density results primarily in a shift from the N-$[HOSi]_4$ to the N-$[HOSi]_3$ populations, which exchange slowly.

If these inferences are correct, they predict that diffusion of smaller polyaromatic hydrocarbons, such as anthracene, should occur at approximately the same rate as that of naphthacene, but the mobile fraction should be close to unity since the maximum number of contacts with the surface is three. Conversely, larger molecules, such as pentacene, can make as many as five surface bonds and the mobile fraction should be very low. Our experimental system does not presently permit investigation of the diffusion of probes which absorb at wavelengths below 450 nm (due to the limitations of the Argon ion laser), so we have been unable to investigate the diffusion of smaller polyaromatic hydrocarbons. Experiments with pentacene are in principle possible but are more difficult because of ease of oxidation and limited solubility in suitable solvents. This work is in progress.

Summary

Changing the level of hydration and hydroxylation allows for qualitative and quantitative comparisons of interaction parameters between the surface and an adsorbed aromatic hydrocarbon. Many microcrystals are observed on surfaces with very low water or silanol content, or with high water content (10%). These results indicate that water will block potential binding sites. These sites also are removed by heating. Reduction in the number of these binding sites, by heat treatment, increases the rate of desorption of naphthacene. These qualitative observations provide more evidence for the well-established idea that binding of aromatic hydrocarbons to silica must involve surface silanol groups (and π electrons in the aromatic rings).

For all samples studied in detail the diffusion coefficient was found to be the same. This indicates that there is only one population of naphthacene that is mobile on the surface. The mobility of this species appears to be lower than that estimated from photochemical and photophysical experiments, which may be due to a difference in sensitivity to short distance motion in these latter experiments compared to the micrometer translations measured here. The diffusion coefficient is reasonable in view of the corresponding values measured for naphthacene in myristoyl coated beads and in membranes. The measurements also reveal that a significant fraction of naphthacene is immobile. The relative amount of the mobile and immobile populations varies with water and silanol content. We attribute this variation to the change in the fractions of naphthacene molecules that are bound to three and four silanols simultaneously. Those bound to three silanols would be mobile while those bound to four would not.

Registry No. H_2O, 7732-18-5; naphthacene, 92-24-0.

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