these defect sites were formed with inert gas ion bombardment. Identical sites are apparently created by vacuum annealing an oxidized polycrystalline titanium foil. These sites not only dissociate water but also can dissociate carbon dioxide. Therefore, under moderate pressure methanation conditions, H_2O and CO_2 produced would subsequently readsorb on the titania and oxidize any Ti^{3+} cations originally produced during reductive pretreatments. This does not preclude the possibility, however, that under reaction conditions an oxidation–reduction process occurs so that at steady state a small concentration of Ti^{3+} sites may exist on the catalyst surface.

Conclusions

Temperature-programmed desorption from well-characterized titania surfaces of systematically varied oxidation state indicated that (i) CO adsorbs weakly with low saturation coverage on oxidized titania, with slight increases in adsorption strength and coverage with increasing extent of surface reduction, (ii) oxidized or reduced titania cannot dissociate H_2, and hence does not adsorb hydrogen strongly in the absence of a source of H atoms, and (iii) CO_2 and H_2O oxidize reduced titania, releasing CO and H_2, respectively.

These results suggest that reactants directly adsorbed on titania do not play an important role in CO hydrogenation for titania-supported catalysts, except possibly as a source of hydrogen adatoms. Second, reduced Ti^{3+} cations become oxidized by product gases (CO_2, H_2O) under normal methanation conditions and hence cannot be important in the enhanced activities observed for titania-supported metal catalysts.

Acknowledgment. We gratefully acknowledge the financial support of Eastman Kodak who provided a fellowship for G.B.R. Funding from the National Science Foundation was also received and is appreciated.

Registry No. Ti, 7440-32-6; TiO_2, 13463-67-7; CO_2, 124-38-9; CO, 630-08-0; H_2, 1333-74-0; H_2O, 7732-18-5.

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Surface Perturbation of Vibrational Transitions of Pyrenesilanes Bound to Silica Gel

M. L. Hunnicutt, J. M. Harris,*
Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

and C. H. Lochmüller
Department of Chemistry, Duke University, Durham, North Carolina 27706 *(Received: April 29, 1985)*

Enhancement of weakly allowed vibrational transitions is reported for pyrenesilane molecules covalently bound to porous microparticulate silica. The appearance of these new bands is attributed to adsorptive interactions which alter the symmetry and electron density of the surface bound molecules. The intensity of the surface-perturbed vibrational modes is shown to vary as a function of the bound silane surface concentration and the water content of the chemically modified silica. Thermal pretreatment of the modified silica produces large intensity differences indicating that the proton-donor properties of surface silanols are significantly influenced by the concentration of surface adsorbed water. Differences in the orientation and associative interactions of bound and surface adsorbed molecules are also inferred.

Introduction

Infrared spectroscopy has been used extensively to investigate adsorptive interactions between molecules and surface hydroxyls (silanols) on porous silica gel. Considerable effort has focused on establishing the physical state of adsorbed molecules as well as the changes in symmetry, orientation, and rotational motion of molecules in the field of the adsorbent. Spectroscopic studies of molecules adsorbed on porous particulates and metal surfaces have shown that electrostatic field gradients at adsorptive surfaces can induce infrared activity of vibrational modes that are normally infrared inactive.[1-9] The enhancement of weakly allowed vibrational transitions and the appearance of new bands where symmetry-forbidden transitions exist has also been observed for pyrene in the presence of polar solvents and has been attributed to a reduction in symmetry of the pyrene molecule via solvent complex formation.[10,11] Similar results could be expected for pyrene adsorbed on porous, microparticulate silica gel.

The present work describes the Fourier transform infrared-photoacoustic spectroscopy of 10-(3-pyrenyl)decyldimethylmonochlorosilane (3PDS) and 3-(3-pyrenyl)propyldimethylmonochlorosilane (3PPS) covalently bound to microparticulate silica gel. New absorption bands were observed in the photoacoustic spectra of the bound pyrene molecules; these bands correspond to weakly allowed transitions not observed in the neat infrared spectra of the 3PDS or 3PPS silanes. The enhancement of these vibrational transitions is attributed to a reduction in symmetry of the pyrene moiety as a result of complex formation with surface silanols. The intensity of these bands varies as a function of the bound silane surface concentration and the water content of the chemically modified silica. Intensity differences of surface-enhanced vibrational transitions are observed for 3PDS and 3PPS silicas having equivalent silane surface coverages. These differences indicate that the bound 3PDS molecules are less sterically hindered and more free to complex with the underlying surface silanols than the shorter chained 3PPS silane. Little vibrational enhancement was observed for pyrene absorbed at surface coverages of less than or equal to one monolayer. This result was unexpected and reflects differences in the associative interactions of the molecules on the silica surface. The results presented yield valuable information concerning molecular perturbations caused by adsorptive surface interactions as well as

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differences in the organization and distribution of molecules adsorbed and bound to porous silica gel.

Experimental Section

Silane Synthesis. 10-(3-Pyrenyl)decyldimethylmonochlorosilane, 3PDS. All glassware was flame-dried under a stream of dry nitrogen and the reactions were carried out under positive nitrogen pressure. Alkylation of 3-bromopyrene (Alfa) was carried out in a round-bottom flask (RBF) equipped with a reflux condenser, rubber septum, nitrogen inlet, and a Teflon stir bar. Anhydrous ether (40 mL) was transferred via cannula to a RBF containing 4 mmol of 3-bromopyrene. The solution was cooled to 0 °C and 4.3 mmol of *n*-butyllithium (Alfa) was slowly added via syringe; 3-lithiopyrene rapidly precipitates out of solution. The reaction mixture is refluxed for 1 h and then cooled to room temperature. A 3 mmol excess of 9-decenyl 1-bromide is added to the reaction mixture and the solution is refluxed for 6 h. The mixture is washed with a saturated aqueous ammonium chloride solution (3 × 100 mL) and the organic layer is collected and dried over anhydrous sodium sulfate. The ether is removed under reduced pressure and the product (9-(3-pyrenyl)decene) is isolated via column chromatography, (silica/hexane). The product is a yellow, viscous liquid: yield 24%.

Hydrosilyation of 9-(3-pyrenyl)decene is carried out in a reaction flask identical with the one previously described. Dry toluene (5 mL) is added to the reaction flask containing 1 mmol of 9-(3-pyrenyl)decene). A 2 mmol excess of dimethylmonochlorosilane (Aldrich) is added, and the mixture is warmed to 30 °C. A syringe delivers 20 μL of a 0.1 M chloroplatinic acid/2-propanol solution, and the reaction mixture was slowly heated to reflux for 4 h. The anti-Markovnikov addition of the silicon hydride to the double bond was extremely exothermic. The product (10-(3-pyrenyl)decylmonochlorosilane) is isolated via vacuum distillation (260–270 °C/0.08 mmHg) as a light-yellow solid at room temperature: yield > 95%.

3-(3-Pyrenyl)propyldimethylmonochlorosilane, 3PPS. Identical reaction conditions were used to form the pyrenylpropylsilane. Allyl bromide (Aldrich) was used to alkylate 3-lithiopyrene to produce 3-allylpyrene: yield 35%. 3-(3-Pyrenyl)propyldimethylmonochlorosilane (195–200 °C/0.09 mmHg) is a viscous yellow liquid at room temperature: yield > 95%.

9-Decenyl 1-Bromide. Bromination of 9-decen-1-ol (Aldrich) was accomplished by forming the sulfonic ester of 9-decen-1-ol followed by nucleophilic displacement of the sulfonic ester by bromine. 9-Decen-1-ol (40 mmol), triethylamine (40 mmol, Aldrich), and 100 mL of dichloromethane (MCB) were added to a 250-mL RBF equipped with an addition funnel, Teflon stir bar, and nitrogen inlet. Methanesulfonyl chloride (45 mmol, Aldrich) was slowly added to the reaction mixture at 0 °C. The mixture was stirred at room temperature for an additional 45 min after addition was completed. The reaction mixture was washed with 200 mL of deionized water, 10% HCl, saturated $NaHCO_3$, and saturated NaCl. The organic layer was collected and dried over anhydrous sodium sulfate. Dichloromethane was removed under reduced pressure to yield a clear, colorless liquid (9-decenyl 1-mesylate): *yield* > *95%.*

A 3 mol excess of lithium bromide (Alfa) was added to a rapidly stirred solution of 9-decenyl 1-mesylate in 100 mL of acetone in a 250-mL RBF under positive nitrogen pressure. Formation of the lithium mesylate precipitate was observable 5 min after addition, and the reaction was stirred for 12 h. The reaction mixture was extracted with dichloromethane and was washed (3 × 150 mL) with a saturated NaCl solution. The organic layer was dried with anhydrous sodium sulfate and the solvent was removed under reduced pressure to yield a clear, colorless liquid (9-decenyl 1-bromide): yield > 95%.

Bonded Phase Synthesis and Photoacoustic Pretreatment. The silica gel used was Whatman Partisil 10 (N_2 surface area of 323 m^2/g, mean pore diameter of 93 Å, and a mean particle diameter of 10 μm). The silica derivatization procedure and subsequent treatment of the chemically modified silica are detailed in a previous report.[12] The surface concentration ($\mu mol/m^2$) of bound silane was determined by elemental analysis and the calculation method of Unger et al.[13]

All silica samples were heated at 70 °C/10 mtorr for 15 min prior to photoacoustic analysis unless stated otherwise. The photoacoustic cell and silica sample were sealed in a glovebag that had been purged continuously for at least 1 h prior to sample preparation. Positive N_2 pressure was maintained and the glovebag was purged for 20 min prior to loading the sample into the photoacoustic cell. The cell was sealed in the glovebag and immediately transferred to the N_2-purged optical bench of the infrared spectrometer.

Photoacoustic Spectra. All photoacoustic spectra were acquired on a Nicolet 7199 Fourier transform infrared spectrometer (FT-IR) modified for photoacoustic detection.[14] The photoacoustic cell is a home-made stainless steel cell specifically designed for use in the Nicolet 7199 spectrometer.[15] The infrared radiation modulated by the interferometer was focused through the cell window onto the chemically modified silica gel. Acoustic waves arising from the periodic heating of the sample were detected via a Bruel and Kjoer 4165 microphone. The signal from the microphone was amplified to a level appropriate for signal processing by the Nicolet computer. The photoacoustic interferograms were collected, averaged, and transformed by the Nicolet 7199 standard software to produce the FT-IR/PAS spectra. All spectra were ratioed to the triglycerine sulfate detector. The mirror velocity of the FT-IR was set at 0.074 cm/s corresponding to a frequency range of 59.2–592 Hz for 400–4000-cm^{-1} incident radiation. All spectra have 2-cm^{-1} resolution.

Diffuse Reflectance Spectra. The diffuse reflectance spectra were acquired on an IBM Series IR/95 FT-IR spectrometer modified with a Harrick Scientific Model DRA-2CN diffuse reflectance attachment. The mirror velocity of the interferometer was set at 0.396 cm/s and all spectra were collected at 4-cm^{-1} resolution by using a mercury cadmium telluride detector cooled with liquid nitrogen. All spectra were referenced to potassium chloride by using the Kubelka-Munk equation.

Fluorescence Spectra. All spectra were collected with a Farrand Model MK-1 spectrofluorometer. All samples were packed into a quartz column flow cell described previously.[12] Emission spectra were collected with the excitation monochrometer set at 310 nm. Excitation spectra were collected with the emission monochrometer set at 380 and 470 nm to monitor monomer and excimer emission, respectively. Corning glass filters, 7–54, and 4–96, were used to eliminate stray radiation from the excitation and emission monochrometers, respectively. The large molar absorptivity of pyrene and the high concentration of the bound pyrene ligands necessitated diluting the chemically modified silica with untreated Partisil 10 (1:1000 by weight) to avoid inner-filter effects in the excitation spectra of the 3PDS silica in contact with H_2O. No sample dilution was necessary for excitation or emission spectra of the dry silicas due to the efficient light scattering of the dry samples.

Results and Discussion

Surface-Perturbed Vibrations for Pyrenesilane Covalently Bonded to Silica. Photoacoustic spectra for 3PDS bonded to Partisil 10 at surface concentrations of 0.46 and 0.68 $\mu mol/m^2$ are shown in Figure 1. New vibrational bands are observed between 1350 and 1725 cm^{-1}; these bands are not present in the infrared spectrum of 3PDS (Figure 2) or the photoacoustic spectrum of underivatized Partisil 10 (Figure 3). The new vibrational band at 1697 cm^{-1} is also seen in the diffuse reflectance spectra of the 3PDS samples (Figure 4) indicating that spectral artifacts originating from the acoustic or photothermal properties of these samples are not responsible for the new vibrational transitions observed in the photoacoustic spectra. Saturation

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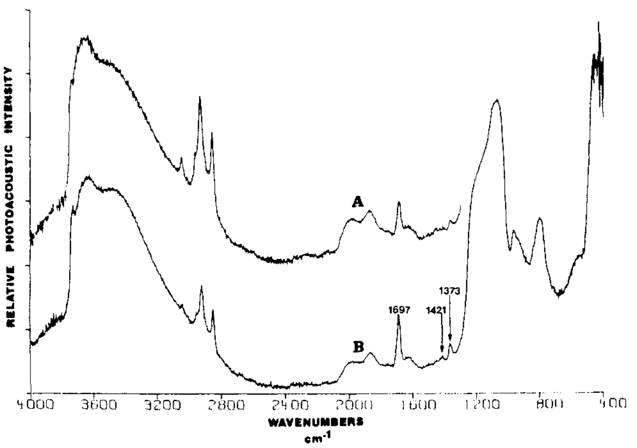

Figure 1. Photoacoustic spectra of 3PDS bound on Partisil 10: A = 0.68 μmol/m^2; B = 0.46 μmol/m^2.

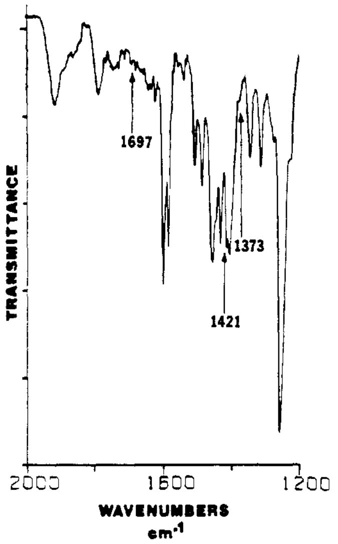

Figure 2. Infrared spectrum of unbound 3PDS.

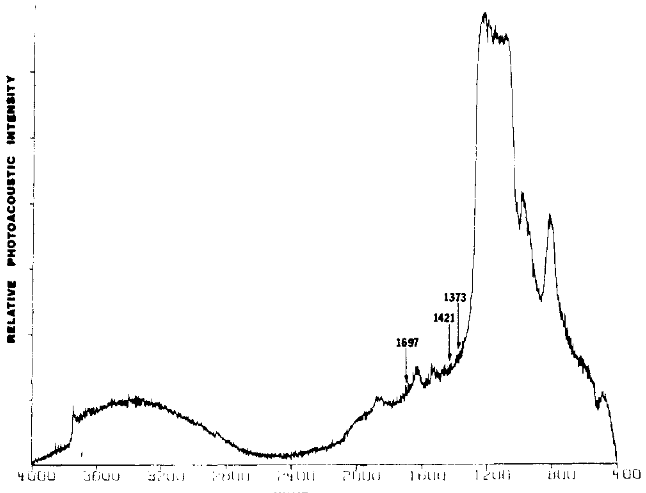

Figure 3. Photoacoustic spectrum of underivatized Partisil 10 unratioed spectrum).

effects, due to the strongly absorbing Si–O–Si stretch, did not permit the new bands at 1373 and 1421 cm^{-1} to be observed by diffuse reflectance.

The band at 1697 cm^{-1} in Figure 1 is shifted to higher frequency relative to the 1688-cm^{-1} band observed by Lianos and Georghiou in the infrared spectrum of pyrene in *n*-heptane.[10,11] Based on previous vibrational analyses for pyrene,[16,17] the 1697-cm^{-1} band can be assigned to the B_{3u} symmetry species and appears to be the first overtone of a ring deformation mode. The band broadening and the 9-cm^{-1} shift of this band to higher wavenumber relative to the 1688-cm^{-1} value are consistent with complex formation. Although the bands observed at 1373 and 1421 cm^{-1} are most probably associated with the pyrene ring system, no definitive assignment can be made.

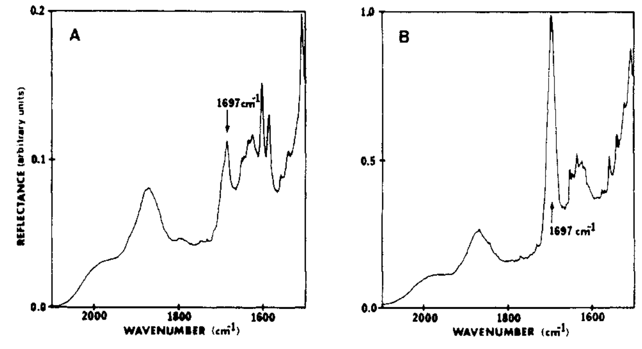

Figure 4. Diffuse reflectance spectra of 3PDS bound on Partisil 10: A = 1.66 μmol/m^2 3PDS; B = 0.14 μmol/m^2 3PDS.

TABLE I: Relative Photoacoustic Intensity[a] for 3PDS and 3PPS[b] Bonded on Silica Gel

	surf. concn, μmol/m^2	relative photoacoustic signal			
		arom C=C vibrn		aliph C–H vibrn	
		1373 cm^{-1}	1697 cm^{-1}	2858 cm^{-1}	2928 cm^{-1}
3PDS	0.14	0.41	0.74	0.03	0.05
	0.19	0.36	0.71	0.07	0.10
	0.32	0.31	0.68	0.22	0.30
	0.46	0.32	0.66	0.38	0.48
	0.60	0.36	0.65	0.68	0.84
	0.68	0.28	0.59	0.81	1.00
3PPS	0.20	0.13	0.36		
	0.33	0.07	0.20		
	0.57	0.08	0.23		

[a] Normalized to 2928-cm^{-1} C–H band intensity for the highest coverage 3PDS sample. [b] Aliphatic C–H bands not distinguishable from silica background.

The appearance of these new vibrational bands in the photoacoustic spectra is believed to arise from adsorptive interactions with surface silanols which alter the electron density and symmetry of the surface bound molecules. A redistribution of electron density would be predicted to lower the symmetry of the surface bound molecules and enhance weakly allowed vibrational transitions that are normally infrared inactive via symmetry perturbation. Molecular complex formation between pyrene and aliphatic alcohols has previously been shown to produce similar intensity enhancement.[10,11] Several experimental parameters which could influence either the bound ligand accessibility to surface silanol regions or the magnitude of surface silanol ionization were investigated to determine the origin of the observed surface-perturbed vibrational modes. The effects of bound ligand surface concentration, steric effects, coadsorbents, and surface dehydration are discussed in the following sections. Differences in vibrational enhancement for adsorbed pyrene vs. surface bound pyrenesilane are also presented.

Influence of Surface Concentration and Steric Effects on Surface-Perturbed Vibrational Intensity. The photoacoustic spectra in Figure 1 show that the aliphatic and aromatic C–H stretching modes at 2858, 2928, and 3047 cm^{-1} increase with increasing 3PDS surface concentration. The surface-enhanced vibrational modes at 1373, 1421, and 1697 cm^{-1}, in contrast, show anomalous behavior and decrease in intensity with increasing surface concentration. Table I shows the effect of concentration on the relative photoacoustic intensity of the surface-enhanced

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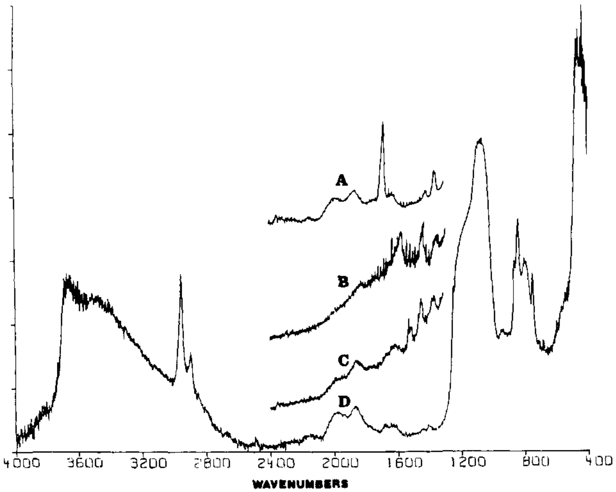

Figure 5. Photoacoustic spectra of 0.19 μmol/m² 3PDS following secondary chemical modification: A = 0.19 μmol/m² 3PDS; B = A + adsorbed *n*-butylamine; C = A + adsorbed *n*-butyl alcohol; D = A + 2.1 μmol/m² TMCS.

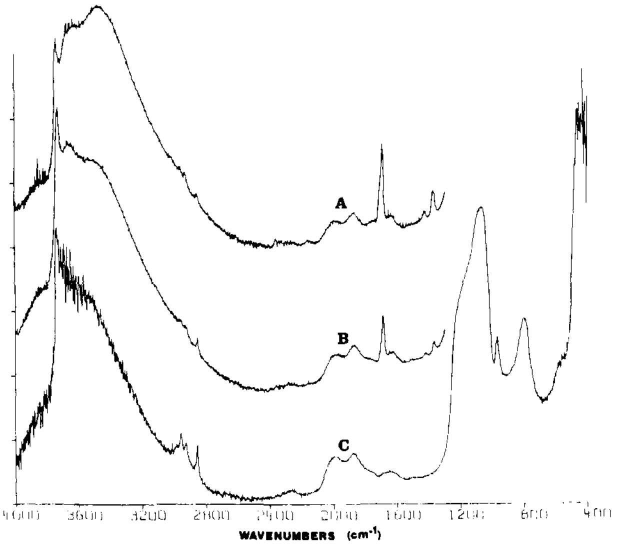

Figure 6. Photoacoustic spectra of 0.19 μmol/m² 3PDS following thermal pretreatment: A = 70 °C/10 mtorr/15 min; B = 150 °C/10 mtorr/1 h; C = 200 °C/10 mtorr/8 h.

transitions compared to the normal behavior of the C–H stretching intensities. The observed decrease in intensity of the surface-perturbed modes reflects a reduction in surface silanol–3PDS complex formation as the accessible silanol concentration is reduced at higher 3PDS surface coverages. Steric effects due to increased crowding of the ligands at higher coverages and the onset of pyrene–pyrene interactions, as discussed below, may also contribute to the observed loss in intensity of the surface perturbed vibrations.

Large intensity differences are observed in Table I for 3PDS and 3PPS silicas of nearly equivalent surface coverages. These intensity differences indicate that the 3PDS molecules are less sterically hindered and more able to complex with the underlying surface silanols than the shorter chain 3PPS molecules. Space filling models of the bound 3PPS molecules show significantly fewer surface contacting configurations relative to the 3PDS molecules. Excimer formation rates of surface bound 3PDS and 3PPS molecules have been found to reflect differences in mobility as predicted by the space filing models and are consistent with the intensity differences observed in Table I.[18]

Influence of Coadsorbents and Surface Dehydration on Surface-Perturbed Vibrational Intensity. Further evidence supporting surface silanol–3PDS complexation is presented in Figure 5. The surface-perturbed vibrational bands undergo significant losses in intensity as a result of secondary chemical modification of the silica surface. Adsorbed *n*-butylamine and *n*-butyl alcohol interact strongly with surface silanols via hydrogen bonding and cannot be displaced by the less polar 3PDS molecules. Exhaustive derivatization of the surface with trimethylchlorosilane yields similar results. As a result, accessible surface silanols which are preferentially derivatized are no longer available for complex formation.

Thermal pretreatment of the 3PDS silicas would also be expected to affect the extent of silanol–3PDS complexation since the chemical properties of silica are significantly altered by the adsorbed water content and surface silanol concentration. Thermogravimetric and infrared measurements have shown that the amount of surface adsorbed water rapidly decreases with increasing temperature and is negligible at temperatures greater than 250 °C.[13,19] Reversible dehydroxylation of the surface silanols subsequently occurs at higher temperatures up to 450 °C.

The influence of surface dehydration on the intensity of the surface-perturbed vibrations is illustrated in Figure 6. Thermal pretreatment of the 0.19 μmol/m² 3PDS silica at 200 °C for 8 h (trace C) completely extinguishes the surface-enhanced modes. Fripiat and Uytterhoeven have reported that the concentration of surface water present under these conditions is approximately 6×10^{-5} mol of H_2O/g of silica.[20] Scott and Traiman have reported that Partisil 20 silica gel equilibrated at 23 °C with an atmosphere of 50% humidity contains 4.3×10^{-3} mol of H_2O/g of silica.[21] Trace C in Figure 6 therefore represents a surface with less than 2% surface adsorbed water. The relative intensity change observed in Figure 6 of the 3462-cm^{-1} band, corresponding to surface adsorbed water, is consistent with this estimate. The bands at 3738 and 3649 cm^{-1} represent "isolated" and "hydrogen-bonded" surface silanols.[13] Rehydrating the surface by boiling the thermally pretreated 3PDS silica in water for 2 h restores the original vibrational intensity (±10%) observed for the 0.19 μmol/m² 3PDS silica prepared at ambient conditions (trace A). Thermally pretreating the silica at intermediate conditions results in a 50% reduction in observed intensity (trace B). These results indicate that surface silanols, in the absence of adsorbed water, cannot account for the observed intensity enhancement of the weakly allowed vibrational transitions. The effect of adsorbed water on the vibrational behavior of the 3PDS silicas is due to the adsorbed water either: (1) enhancing the acidity of surface silanols, or (2) intensifying the electrostatic field at the surface of silica gel.

Several spectroscopic studies have shown that the adsorption of water significantly increases the proton-donor properties of synthetic zeolites.[19] Enhanced proton-donor properties could similarly be expected for silica gel although the surface composition responsible for the acidic properties of zeolites is different from those of porous silica. Anderson and Parks have shown that the electrical conductivity of silica is nonohmic and is strongly dependent on the concentration of surface adsorbed water.[22] Proton dissociation and electrical conductivity are enhanced by the adsorption of polar molecules which reduce the dissociation energy of the surface hydroxyl protons. Thus, the adsorption of water would be expected to increase the acidity of surfaces silanols and the electrostatic field at the silica surface as a result of increased proton dissociation and surface conductivity. Sheppard and Yates have estimated the field at the surface of porous silica by comparing perturbations of spectroscopic transitions for hydrogen adsorbed on silica and gaseous hydrogen in a strong electric field.[1,23]

Infrared reflectance measurements of pyrene adsorbed onto an electrode surface could provide a definitive test of the electric field

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TABLE II: Relative Photoacoustic Intensity[a] for Pyrene Adsorbed on Silica Gel

surf. concn,[b] μmol/m^2	arom C=C vibrn, 1697 cm^{-1}
0.38	0.06
0.75	0.07
1.49	0.03
4.51	0.00

[a] Normalized to 2928-cm^{-1} C–H band intensity of the highest coverage 3PDS sample. [b] Monolayer coverage is based on the calculate maximum surface area of a pyrene molecule (110 Å) and the surface area of Partisil 10 (323 m^2/g). Crystallographic data was used to calculate the maximum surface area occupied by pyrene.[27,28]

origin of the surface-enhanced vibrational modes observed in the photoacoustic spectra of the 3PDS and 3PPS silicas. Pons and Korzeniewski have recently observed field-induced infrared adsorption at 1648 cm^{-1} for pyrene adsorbed at a Pt electrode surface.[7] This normally infrared inactive absorption band was assigned to the totally symmetric (A_g) stretching mode of pyrene. A redistribution of electron density due to the intense electric field generated at the electrode surface distorts the symmetry of the pyrene molecule to allow the otherwise infrared inactive transition to be observed. Although electric field-induced effects may be present on the silica surface, the lack of field-induced absorption bands at 1373, 1421, and 1697 cm^{-1} in the electrode reflectance spectra demonstrates that these surface perturbed vibrations are not due to field effects, but probably arise from surface complexation.

Surface-Perturbed Vibrational Intensity of Adsorbed Pyrene. Surface complexation and the corresponding appearance of new vibrational modes would also be expected for pyrene adsorbed on silica gel due to its larger polarizability relative to the substituted pyrenesilane. The relative photoacoustic intensity values for pyrene adsorbed on Partisil 10 are presented in Table II and show a weak signal for the complex at surface coverages of less than or equal to one monolayer. No surface complex band was observed at concentrations greater than one monolayer. The intensity observed for adsorbed pyrene compared to bound pyrenesilane at nearly equivalent surface concentrations was unexpected and must reflect differences in the physical state or associative interactions of the molecules on the silica surface.

Ware and co-workers have shown that pyrene adsorbed on silica gel at surface coverages as low as 0.01 μmol/m^2 exhibits significant bimolecular ground-state (pyrene–pyrene) association which leads to "excimer-like" emission at 470 nm.[24] The emission spectra for adsorbed pyrene and bound 3PDS at nearly equivalent surface concentrations are shown in Figure 7. The large difference in the excimer-to-monomer intensity ratios, (E/M = 2.8, adsorbed pyrene; E/M = 0.09, bound 3PDS), indicate that adsorbed pyrene molecules preferentially associate with each other rather than forming pyrene–surface silanol complexes characteristic of surface bound 3PDS molecules. Thus, bimolecular ground-state association of adsorbed pyrene efficiently competes with pyrene–surface silanol complexation and accounts for the intensity differences observed at 1697 cm^{-1} between the adsorbed and bound pyrene molecules.

Excitation spectra were also obtained for the 3PDS silicas to determine if bimolecular ground-state association competes with surface silanol–pyrenesilane complexation as a function of surface water content. Excitation spectra characteristic of bimolecular ground-state association were observed for dry 3PDS samples and were identical with those by Ware and co-workers.[25],[26] In contrast, excitation spectra collected for 3PDS silicas in contact with H_2O indicated no evidence of bimolecular ground-state complexation and were identical with the excitation spectra reported by Lochmüller and co-workers.[12] These results suggest that bimolecular ground-state association is favored at anhydrous or low surface water conditions, while surface silanol–pyrenesilane complexation predominates as the water content of the surface increases. The influence of surface dehydration on the intensity of the surface-perturbed vibrations shown in Figure 6 is consistent with this hypothesis.

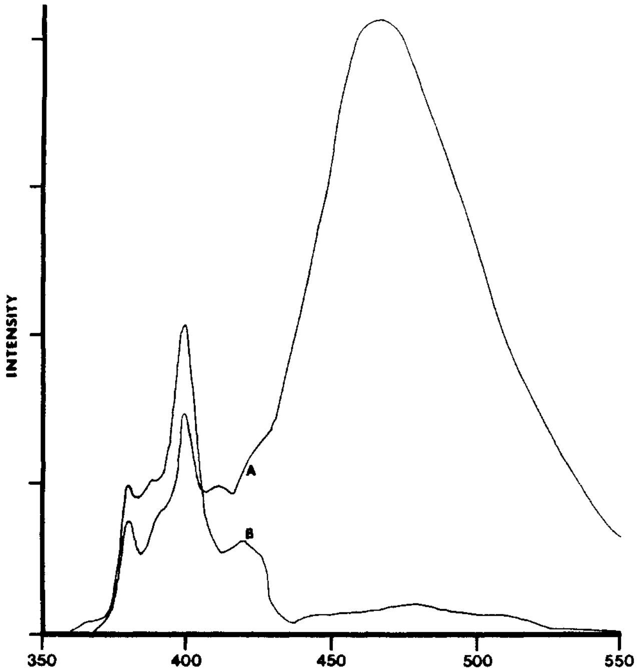

Figure 7. Fluorescence emission spectra of pyrene adsorbed and 3PDS bound on silica gel: A = reproduced with permission from ref 25, 0.14 μmol/m^2; B = corrected spectrum of dry 0.19 μmol/m^2 3PDS silica.

Conclusions

Molecular complex formation between bound pyrenesilane molecules and surface silanols results in the appearance of strong, new vibrational bands in the photoacoustic spectra of 3PDS and 3PPS silicas. The appearance of these surface-enhanced modes was shown to be due to adsorptive interactions which alter the electron density and symmetry of the bound molecules. It may be possible for weakly allowed modes to acquire considerable vibrational intensity through resonance with allowed vibrations of the same symmetry class once the symmetry of the surface bound molecule has been distorted. Although this offers a possible explanation for the enhancement of surface-perturbed vibrational transitions, it does not adequately explain the specific requirement of surface silanol–pyrenesilane complexation to observe the effect. The apparent chemical specificity of the intensity enhancement indicates a need for more detailed models of adsorptive surface interactions and their perturbation of the vibrational properties of bound and adsorbed molecules.

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Registry No. 3PDS, 98689-69-1; 3PPS, 86278-57-1; 9-decenyl-1-bromide, 62871-09-4; 9-(3-pyrenyl)decene, 98689-70-4.

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