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Determination of Hydrogen-Bonding Acid Sites on Silica Using the Cal-Ad Method

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Abstract: Silica gel, under various hydration conditions, was investigated using a novel calorimetric adsorption (Cal-Ad) method. This method combines data from calorimetric and adsorption titrations of a solid surface using a small probe molecule in a noninteractive solvent. The Cal-Ad method proved to be more sensitive than other characterization techniques (e.g. temperature-programmed desorption) and calorimetric techniques. Previously, it was believed that the silica surface consisted of one type of hydrogen-bonding site. The Cal-Ad method has elucidated three hydrogen-bonding sites of different strengths using pyridine as the basic probe molecule. The equilibrium constant of binding, enthalpy of binding, and number of each of these sites have been determined.

Introduction

The characterization of solid acids and bases has become an area of increasing interest in recent years because of their applications in heterogeneous catalysis.[1] The characterization of acid/base sites on solid surfaces is recognized as a difficult task. Shifts in infrared bands of coordinated molecules were measured and proposed to reflect acid strengths.[2,3] More recently, nuclear magnetic resonance spectroscopy has been used to study the coordination of donor molecules to the surface.[4–6] Temperature-programmed desorption (TPD) is another technique which has gained increasing use as an indicator of the acidity of solid acids.[7] The use of calorimetry in the past has been limited mostly to the adsorption of gaseous bases onto solids.[8] Recently, solution calorimetry has been used to measure the total heat evolved when donors are added to solid acids.[9,10] This provides an enthalpy in units of kilocalories per mole of donor added. These measurements are difficult to interpret because the heat evolved has contributions from the amount of base complexed (i.e. the equilibrium constant), the enthalpy, and number of sites involved. A full characterization of the solid acid would involve measuring the equilibrium constant and enthalpy of adduct formation for each of the different acceptor sites of the solid. None of the above approaches provide this information. Thus, it is not surprising to find that the measured values from most of these procedures fail to parallel catalytic activity.

One of the more recent approaches to characterizing solid catalysts, the Cal-Ad method, has been used[11] to successfully distinguish two different sites for coordination of donors to a Pd/carbon heterogeneous catalyst. Conventional calorimetric (differential scanning calorimetry) and desorption (thermal gravimetric analysis) techniques could not distinguish the sites and provided average values for interaction with the two sites. In this paper, the Cal-Ad method has been improved and has provided an unprecedented characterization of the different types of sites and the quantity of each type of site found on silica. In addition, the free energy of binding to each different site is determined along with the enthalpy for binding to each site in units of kilocalories per mole of adduct.

Silica was chosen as the solid acid for this study because of its extensive use as a support in heterogeneous catalysis, in separations, and in microelectronic fabrication. It has been studied extensively by infrared spectroscopy[12] and nuclear magnetic resonance spectroscopy.[13] Previous calorimetric investigations[9,10] of silica bonding to donor molecules assumed only a single binding site for a base binding to the silica surface and, in one study,[10] complete complexation to this site. In the absence of equilibrium data, the units for such measurements are kilocalories per mole of donor added. If more than one site is involved, the enthalpy corresponds to an average of the fraction of the pyridine coordinated by the two sites. Model studies on silsesquioxanes[14] have shown that sites of differing reactivity should be present depending on the extent of hydrogen bonding between neighboring hydroxyls on the surface. Isolated silanols are less acidic than clusters possessing at least three mutually hydrogen bonded hydroxyl groups.

Using the Cal-Ad method we can determine equilibrium and enthalpy data for different sites on Fisher silica gel S-679 coordinating to pyridine. Furthermore, we have been able to demonstrate the dramatic influence that pretreatment of the silica has on its reactivity. Comparison of this data with gas phase–solid data demonstrates the magnitude of the nonspecific interactions that are involved when gas phase–solid equilibria are measured.

Experimental Section

Purification of Materials. Fisher silica gel S-679 (Lot No. 903424) was used as supplied. Studies were carried out on samples that were "dried" by evacuating at 28 and 200 °C. BET surface areas of 590 m^2/g were obtained after both pretreatment temperatures.

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[1] Tenabe, K.; Hattori, H.; Yamaguchi, T.; Tanaka, T. *Acid-Base Catalysis*; VCH Publishers: New York, 1989.

[2] Parry, E. P. *J. Catal.* **1963**, *2*, 371.

[3] Curthoys, G.; Davydov, V. Ya.; Kiselev, A. V.; Kiselev, S. A.; Kuznetsov, B. V. *J. Colloid Interface Sci.* **1974**, *48*, 58.

[4] (a) Maciel, G. E.; Haw, J. F.; Chuang, I.; Hawkins, B. L.; Early, T. A.; McKay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529. (b) Dawson, W. H.; Kaiser, S. W.; Ellis, P. D.; Inners, R. R. *J. Phys. Chem.* **1982**, *86*, 867. (c) Duncan, T. M.; Winslow, P.; Bell, A. T. *Chem. Phys. Lett.* **1983**, *102*, 163.

[5] (a) Batamack, P.; Doremieux-Morin, C.; Fraissard, J.; Freude, D. *J. Phys. Chem.* **1991**, *95*, 3790. (b) Batamack, J.; Doremieux-Morin, C.; Vincent, R.; Fraissard, J. *Chem. Phys. Lett.* **1991**, *180*, 545.

[6] Klinowski, J. *Chem. Rev.* **1991**, *91*, 1459.

[7] Fierro, J. L. G. *Spectroscopic Characterization of Heterogeneous Catalysts Part B: Chemisorption of Probe Molecules*; Elsevier: New York, 1990.

[8] Gravelle, P. C. *Catal. Rev.—Sci. Eng.* **1977**, *16* (1), 37.

[9] Fowkes, F. M.; McCarthy, D. C.; Tischler, D. O. *Polymer Science and Technology, Vol. 27 (Mol. Charact. Compos. Interfaces)*; Plenum Press: New York, 1983; pp 401–411.

[10] Arnett, E. M.; Cassidy, K. F. *Rev. Chem. Intermed.* **1988**, *9*, 27.

[11] Lim, Y. Y.; Drago, R. S.; Babich, M. W.; Wong, N.; Doan, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 169.

[12] (a) McDonald, R. A. *J. Phys. Chem.* **1958**, *62*, 1168. (b) Morrow, B. A.; McFarlan, A. J. *J. Non-Cryst. Solids* **1990**, *120*, 61.

[13] Bronnimann, C. E.; Zeigler, R. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 2023.

[14] Feher, F. J.; Newman, D. A. *J. Am. Chem. Soc.* **1990**, *112*, 1931.

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Pyridine (Fisher) was stored over BaO and redistilled over CaH_2 using a 12-in. Vigreux column. Cyclohexane (Aldrich) was treated with activated charcoal three times in order to remove traces of benzene. It was then distilled over P_2O_5 and stored over 4-Å molecular sieves for at least 24 h prior to use.

Reichardt's dye (2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate), 95%, was used as supplied by Aldrich.

Calorimetry and Adsorption. The calorimetric titration was carried out as described previously[11] except samples were not removed for measurement of the free base concentration in solution during the incremental base addition.[15] Instead, the adsorption titration was carried out in a separate reaction vessel using a solution volume and mass of the silica that were both 3 times larger than those employed in the calorimetric titrations. In this way, a smaller fraction of the pyridine could be removed with each sampling of the solution. A series of pyridine additions was made to provide a range in pyridine concentration similar to the range of donor concentration employed in the calorimetric titration (3.5 μM–0.2 M). After each addition, 3-4 min was allowed for equilibration (this is the same time interval as between calorimetry injections), after which time the stirring was stopped to allow the solid to settle. An aliquot of the solution was taken and replaced by an equal volume of pure solvent, and stirring was resumed. The next addition of pyridine was then made and the above procedure repeated. The pyridine concentration of the samples removed was determined by UV/vis spectrophotometry at 251 nm, and the concentration of the pyridine remaining in solution for the adsorption experiment was recalculated.

The purpose of the adsorption titration in the Cal-Ad procedure is to determine the equilibrium concentration of pyridine in solution for each added increment of pyridine in the calorimetric experiment. With the adsorption titration being separate from the calorimetric titration, problems can arise in making a direct comparison of the equilibrium position in the two experiments. The direct comparison is necessary in order to solve the adsorption and calorimetric data simultaneously for the best K. This problem is overcome by using a constant ratio for the volume of solution/mass of solid for both measurements. An adsorption isotherm is constructed from the adsorption titration data which covers the range of base concentrations used in the calorimetric titration. The best-fit isotherm can be calculated using a modified simplex routine designed to solve the following multiple site, Langmuir type equilibrium equation[16] for a series of base concentrations.

$$S_TB = \sum \frac{n_i K_i [B]}{1+K_i[B]} \qquad (1)$$

For i sites, S_TB is the total number of moles of base adsorbed per gram of solid, n_i is the number of moles of site i per gram of solid, K_i is the equilibrium constant of binding at site i, and [B] is the equilibrium concentration of base in solution. In the calorimetric experiment, only the total concentration of base added is known for each calorimetric injection. The total number of moles of base on the solid (S_TB) is expressed as follows:

$$S_TB = \frac{([T] - [B])V}{g} \qquad (2)$$

where [T] is the total molar concentration of injected base and V is the volume of the experiment. By substitution of eq 1 into eq 2 the following relationship is obtained:

$$\frac{([T] - [B])V}{g} = \sum \frac{n_i K_i [B]}{1+K_i[B]} \qquad (3)$$

The equilibrium concentration of base is measured in the adsorption experiment. In order to obtain the equilibrium base concentration for a base addition in the calorimetric experiment, a preliminary Langmuir analysis of the adsorption data is carried out to give K_i and n_i. These values of K_i and n_i are used to calculate the [B] corresponding to the calorimetric measurement. This allows substitution of these [B] values calculated for each base addition along with the heats obtained from the calorimetric titration into the following equation:

$$\frac{h}{g} = \sum \frac{n_i K_i [B]}{1+K_i[B]} \Delta H_i \qquad (4)$$

Two sets of simultaneous equations are written. One set is of the form of eq 4. The second set is of the form of eq 1. Each set includes an equation for each base addition. The two sets are then solved simultaneously for the best values of K_i, n_i, and ΔH_i that reproduce the experimental quantities. It is important to note that the ratio of the volume of solution to the mass of solid (V/g) must be identical in the calorimetric and adsorption experiments. This is necessary to simultaneously solve the combined calorimetric and adsorption data sets for n_i, K_i, and ΔH_i values (i.e. the base concentration in solution relative to the amount of solid must be the same in both experiments).[17] It should also be noted that the concentration range used in the calorimetric titration should be within the concentration range studied in the adsorption titration to avoid uncertain extrapolation of the best-fit adsorption isotherm outside of the measured range.

Table I. Thermodynamic Parameters Obtained in Cyclohexane for Silica–Pyridine Hydrogen Bond Formation

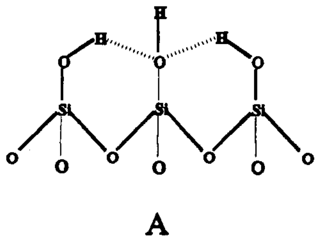
	evacuated at 28 °C	evacuated at 200 °C
n_1 (mmol/g)	0.86	1.12
K_1 (M^{-1})	17 600	25 400
$-\Delta H_1$ (kcal/mol)	12.6	5.5
$-\Delta G_1$ (kcal/mol)	5.8	6.0
ΔS_1 (eu)	−22.8	1.7
n_2 (mmol/g)	0.86	1.30
K_2 (M^{-1})	320	580
$-\Delta H_2$ (kcal/mol)	5.3	3.2
$-\Delta G_2$ (kcal/mol)	3.4	3.8
ΔS_2 (eu)	−6.4	2.0

Ultraviolet/Visible Spectroscopy. All UV/vis spectra were obtained using a Perkin-Elmer Lambda 6 UV/vis spectrophotometer. Suprasil quartz cells of 1- and 10-mm path length were employed in the adsorption studies. For spectra of the solid silica, a mineral oil mull of silica was made on a piece of filter paper and referenced against mineral oil on filter paper.

Fourier Transform Infrared (FTIR) Studies. All FTIR spectra were taken o a Nicolet 5DXB FTIR using a fluorolube grease GR-362 (Fisher) mull or mineral oil (Aldrich) mull and sodium chloride plates.

Results and Discussion

Acidity of Hydrated Silica Gel. The thermodynamic data from the Cal-Ad analysis of the sample evacuated at 28 °C (VAC28) are shown in Table I. Two different reactive sites were found, with the second one being considerably weaker than the first. The enthalpy for pyridine coordination to the first site (A) is −12.6 kcal mol^{-1}, and that for the second site (B) is −5.3 kcal mol^{-1}. The fit of these results to the experimental data points is shown in Figure 1, which illustrates both the adsorption and calorimetric data.



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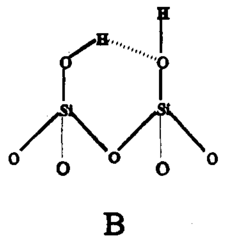

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[15] Previously, both the calorimetric and adsorption studies were done simultaneously in the same reaction vessel. Upon sampling the solution for the adsorption analysis, it was possible that small amounts of the solid were removed from solution. This could lead to a decreasing amount of solid throughout the titration. In order to eliminate this problem, separate calorimetric and adsorption titrations can be used. For the two titrations to be directly correlated, there are considerations which must not be overlooked.

[16] The calculation of the percentage of surface covered by the adsorbed pyridine yields a value of 24.2 and 34.1% maximum total surface coverage for the VAC28 and VAC200 samples, respectively. This result makes the probability of lateral interactions small, justifying the use of the Langmuir treatment.[18]

[17] If this condition is not met, the data sets may be incompatible in terms of the number of different types of distinguishable sites (e.g. at a higher V/g ratio a more reactive site could be averaged in with a less reactive site, which would give rise to a faulty analysis if this data set was then used in combination with a data set obtained at a lower V/g ratio in which the two sites were separable).

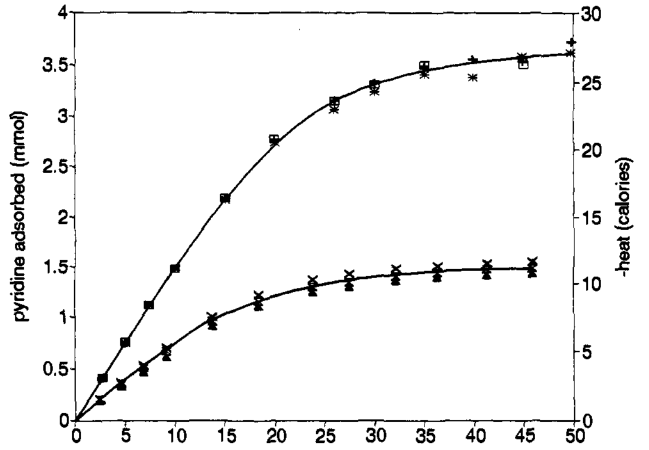

Figure 1. Adsorption isotherm and heat of adsorption vs total pyridine injected for VAC28: □, *, +, adsorption data points; ▲, ×, X, calorimetric data points; solid lines, lines calculated using values from Table I.

In the Cal-Ad analysis, the pyridine concentration ranged from the smallest amount detectable to near saturation of the silica surface. The different reactive sites were discovered because both the amount of pyridine adsorbed and the amount of heat evolved were measured over this large donor concentration range. A further decided advantage of the Cal-Ad method is the determination of the number of active sites as 0.86 mmol g^{-1} for site A and 0.86 mol g^{-1} for site B.

It is interesting to note that a simple Langmuir analysis[18] of this adsorption data yields a different result than that obtained by the Cal-Ad method. The Langmuir equation

$$\frac{[B]}{S_1B} = \frac{1}{n_1K_1} + \frac{[B]}{n_1} \tag{5}$$

is solved by plotting $[B]/S_1B$ vs [B]. The adsorption data produces a straight line, indicating that there is 1.6 mmol/g of a single type of site with an equilibrium constant of 2700 M^{-1}. This is clearly inconsistent with the calorimetric data.[19]

In this system, the possibility exists that the first site involves formation of the hydrogen-bond adduct and the second site involves reaction of this adduct with more pyridine to form $(C_5H_5N)_2H^+$. Accordingly, the reaction between silica and pyridine was probed using FTIR spectroscopy. It has been reported that bands at 1447 and 1599 cm^{-1} for pyridine adsorbed on silica gel are indicative of hydrogen-bonded pyridine.[2] Figure 2 shows the spectrum obtained for a silica sample at the completion of a calorimetric titration as well as the silica surface before reaction. These spectra clearly show that the interaction between pyridine and the silica surface involves a hydrogen-bonded adduct. Pyridinium ion is not formed, for it would be indicated by a characteristic band at 1540 cm^{-1}. The second site which forms in excess pyridine is also a hydrogen-bonded adduct. It is significant to note that the infrared spectrum does not resolve separate shifts for the two adducts in these samples. Furthermore, the pyridine shifts upon hydrogen bonding to the strong site of VAC28 are the same as those for hydrogen bonding to the weaker site of VAC200 (Table I) within experimental error.

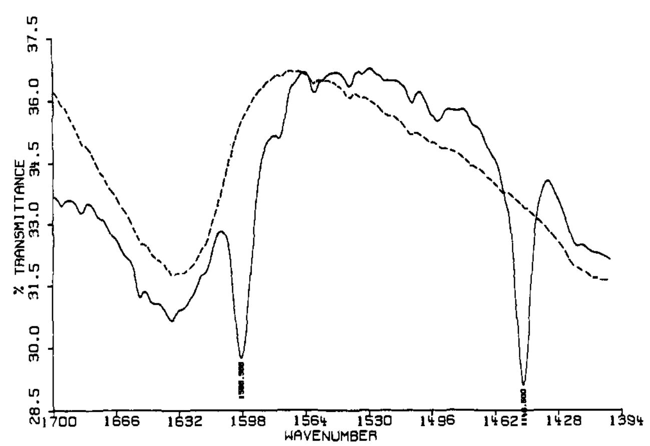

Figure 2. FTIR spectrum of VAC28 in a fluorolube mull (– – –); spectrum of VAC28 after completion of calorimetric titration in a fluorolube mull (—).

Arnett et al.[10] report an enthalpy of –12.37 kcal per mole of pyridine added to a silica slurry in hexane. In order for this value to be an enthalpy of adduct formation it is necessary to show that, at the pyridine concentrations used, all the donor is coordinated and only one site is involved. Comparison of this value with the reported enthalpy for site A in this work indicates the extent to which these assumptions are correct. Base concentrations remaining in solution are not specified in the Arnett study,[10] but at the low base concentrations used in their work most of the donor is coordinated to the first site. Solution enthalpies for pyridine bonding to silica gel reported previously by Fowkes et al.[9] vary from 11.3 to 12.9 kcal mol^{-1}. These values[9] were calculated by correcting for the base concentration remaining in solution. However, at the concentrations studied, our results show that this data[9] has contributions from the second site averaged into the reported enthalpy. This could account for the slightly lower enthalpy values found in some systems. Since these studies were carried out on different types of silica than employed in our study, the similarity in the enthalpies of interaction indicates that similar surface sites give rise to the strong acid centers of the different samples.

Acidity of Dehydrated Silica Gel. The combined Cal-Ad measurements on a sample of silica gel S-679 that was pretreated by heating to 200 °C under vacuum (VAC200) were carried out next. The results of the best-fit analysis show that two different sites exist. The thermodynamic data and the values of *n* have been compiled in Table I. The fit of the calculated concentration and heat evolved to the experimental data was similar to the fits shown in Figure 1. The enthalpy calculated for pyridine hydrogen bonding to the first site on VAC200 is similar to that found for the second site on VAC28 and is therefore attributed to a B type site. The difference in the entropy of adduct formation between the two different samples is very interesting and may be due to an increased propensity of the VAC200 surface to physisorb cyclohexane. The more stringent drying results in a more hydrophobic surface from loss of hydroxyl groups. Dispersion interactions, which are a function of mass, are expected to be larger with silicon and oxygen atoms than with hydrogen atoms. As the number of hydroxyl groups are decreased, hydrophobicity and dispersion interactions increase. When the pyridine hydrogen bonds to the remaining hydroxyl groups of the hydrophobic solid, the surface expulsion of cyclohexane molecules into the bulk solution would lead to a positive entropy.

The above proposal is supported by infrared measurements. The FTIR spectrum of VAC200 was the same as observed for VAC28 in the 1400-1700-cm^{-1} region. An interesting difference in the two spectra was observed in the region above 3000 cm^{-1}.

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(18) Adamson, A. W. *Physical Chemistry of Surfaces*, 3rd ed.; Interscience: New York, 1976.

(19) Problems arise with the Langmuir analysis when there are two different types of adsorption sites present in nearly equal amounts (as is the case here). Since the slope of the line obtained for eq 5 is dependent solely on the number of sites, there will be no change in the slope of the line if the two sites are present in equal quantities. By dividing eq 5 by [B], another linear equation is obtained in which a plot of $1/S_1B$ vs $1/[B]$ should yield another straight line plot. This analysis emphasizes data points taken at lower concentration and, in the pyridine on silica case, shows curvature consistent with the two sites found by calorimetry. It is also important to note that the data points emphasized in this plot are obtained at the lowest concentrations of pyridine and contain the largest experimental error (since the molar absorptivity of pyridine is not large, ϵ_{max} = 2000). This serves to illustrate the difficulty in extracting meaningful data solely from adsorption isotherms.

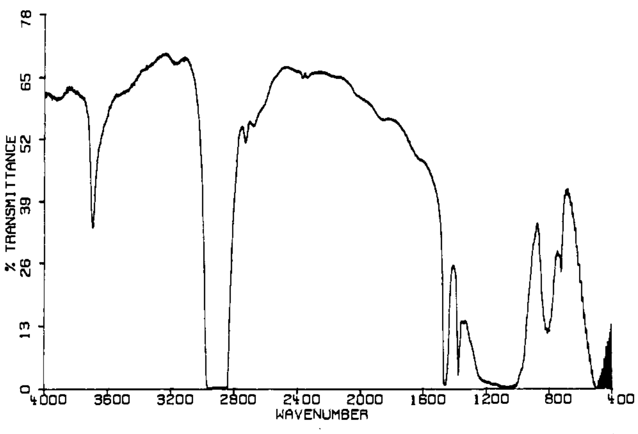


Figure 3. FTIR spectrum of Fisher S-679 (after pretreatment under flowing O_2 at 450 °C) in a mineral oil mull.

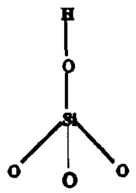
The O–H stretching frequencies for silica, above 3000 cm^{-1}, have been thoroughly studied and are quite informative. The isolated hydroxyl stretching frequencies occur at 3747 cm^{-1} when studied as pellets in evacuated cells.[12] Figure 3 shows a spectrum in a mineral oil mull of a silica sample that was heated to 450 °C under flowing O_2 and then cooled to room temperature. The peak appearing at 3696 cm^{-1} is assigned to an isolated silanol due to its sharpness. Hydrogen bonding leads to a significant broadening of the O–H stretching vibration.

The shift from 3747 cm^{-1} in vacuum to 3696 cm^{-1} in a mineral oil mull is attributed to dispersion forces from physisorbed mineral oil. Absorbances from both the hydrogen-bonded and isolated silanols were present in the spectrum obtained for VAC200. The spectrum of VAC28 was less interesting in this region. Only a large broad peak was observed for the hydrogen-bonded silanols, and no sharp absorbance from isolated silanols was seen.

In order to determine which silanols react first when pyridine is added, VAC200 was titrated and the FTIR spectrum recorded after each addition (Figure 4). A frequency decrease and broadening of the absorbance is expected when hydrogen-bond acceptors coordinate to donors. From these spectra, it is apparent that the first silanols to react are those in the hydrogen-bonded region around 3500 cm^{-1}. Beginning with the addition of the second increment of pyridine, a slight broadening of the isolated silanol absorbance occurs, indicating that they have begun to react. Reaction continues as more pyridine is added, and the isolated silanol vibration broadens extensively. This substantiates our earlier proposal that the hydrogen-bonded silanols are more acidic than the isolated silanols.

An explanation for the difference in reactivity of silanol sites is suggested by solution reactivity studies on silsesquioxanes.[14] The most acidic silanol is found when three adjacent silanols are capable of hydrogen bonding to each other. Our infrared results with incremental pyridine addition indicate that the hydrogen-bonded silanols react first. The strongest site in VAC28 is as, or more, extensively hydrogen bonded than the structure shown in A. The structure in B is assigned to the second site in VAC28 and the first, more acidic, site on VAC200. The isolated silanols C are weaker acids and can be assigned to the second site of VAC200. The structures for sites A, B, and C are the same types of surface species proposed to arise from different pretreatment temperatures by Hench.[20]

There is precedence for a hydrogen-bonding interaction leading to increased acidity. For example, the first ionization constant[21] of maleic acid (*cis*-1,2-ethylenedicarboxylic acid) is 1.4×10^{-2} and that of fumaric acid (*trans*-1,2-ethylenedicarboxylic acid) is 9.3×10^{-4}. Intramolecular hydrogen bonding stabilizes the



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conjugate base and increases the acidity of the cis derivative. A similar interaction is proposed for silanol clusters.

Characterization of the Silica Gels with Betaine. In another attempt to find a spectral probe that would distinguish different strengths of sites on the VAC28 surface, Reichardt's dye was adsorbed onto the silica from a methylene chloride solution. This organic dye has been used as a probe of solvent polarity and is reported to have the largest solvatochromic shift in the ultraviolet/visible region ever observed.[22] The shift in protonic solvents has contributions from a specific hydrogen-bonding interaction and from nonspecific solvation.[22] With silica gel, the different types of sites should shift the longest wavelength band of the dye by different amounts. This should give rise to two different absorption maxima for the lowest energy transition in the dye. Figure 5 illustrates the UV/vis spectra obtained for VAC28 before and after adsorption of the dye. Only one maximum is observed at 492 nm. In view of the broad adsorption bands, this probe is not able to distinguish separate sites. Furthermore, the spectrum of betaine on VAC200 is the same as that of VAC28 within experimental error. Spectra were taken at different loadings of the dye, and though the color intensified with increased loading, the maximum in the spectrum of each sample occurred at the same wavelength. At the lowest loading, the silica was a faint red with a lot of the white silica particles. The red color continued to darken with increased loading until the surface would no longer adsorb any more dye, at which point the red color was so intense that the silica appeared a deep purple. The observed shift of 492 nm corresponds to an $E_T(30)$ value of 58.1 kcal/mol. Since the shifts of VAC28 and VAC200 are the same, betaine must be oriented on the surface in a manner that does not permit the specific hydrogen bonding of its carbonyl group to the silanol. Thus, the nonspecific interaction with the silica surface is more than the combined "polar" interaction with methanol ($E_T(30)$ = 55.4 kcal mol^{-1}) but slightly less than that of 2,2,2-trifluoroethanol (59.8 kcal mol^{-1}) and water (63.1 kcal mol^{-1}).[21] A larger shift occurs for the silica surface than for any polar, non-hydrogen-bonding solvent, e.g. CH_3NO_2 (46.3 kcal mol^{-1}).

Gas–Solid Equilibria. Extensive literature is available describing the use of temperature-programmed desorption, TPD, and differential scanning calorimetry, DSC, to characterize the acidity of solids. As shown in an earlier report,[11] these methods are not as effective as the Cal-Ad method in distinguishing sites of different acidity. Thus, data from these studies often provide values representing a complex averaging of the different interactions. If one tries to correlate reactivity, in an application that involves only the stronger sites on a series of solids, the average value provides little insight concerning the number or strength of reactive sites. A second complicating factor in ascertaining the acid–base component of the reactivity from TPD and DSC involves the added contribution to enthalpies measured with these techniques from nonspecific dispersion interactions. Even in the absence of donor–acceptor interactions, a negative enthalpy will accompany the condensation of a gaseous molecule on a solid surface. This can be larger than the heat of condensation of the gaseous molecule. An indication of the magnitude of the contribution from this effect can be appreciated by comparing

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(20) Hench, L. L.; West, J. K. *Chem. Rev.* **1990**, *90*, 33.

(21) *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., Ed.; CRC Press: Boston, 1990.

(22) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*, 2nd ed.; VCH: Weinheim, Federal Republic of Germany, New York, NY, 1984.

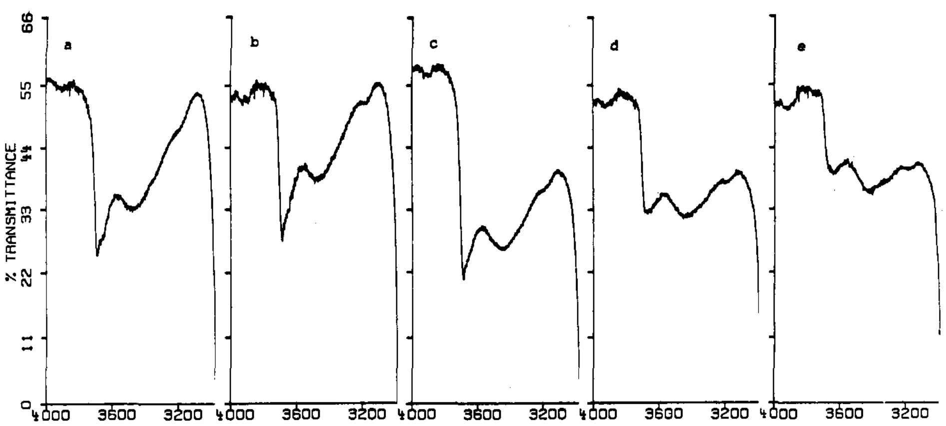

Figure 4. FTIR spectra of Fisher S-679 evacuated at 200 °C: (a) no pyridine added; (b) 0.14 mmol/g pyridine; (c) 0.26 mmol/g pyridine; (d) 0.39 mmol/g pyridine; (e) 0.52 mmol/g pyridine.

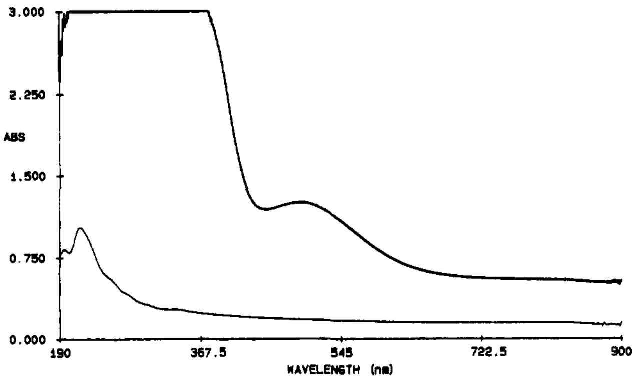

Figure 5. UV/vis spectra of VAC28 (bottom) and VAC28 (top) saturated with Reichardt's dye.

a recently reported enthalpy for a gas phase–solid equilibrium with that reported here for the solution–solid equilibrium.

Dumesic[23] reported an enthalpy of −22.7 kcal mol^{-1} for binding of gaseous pyridine to a sample of solid Cab-O-Sil at 450 °C. A sample of Fisher S-679 silica was pretreated as reported for the Cab-O-Sil sample. This sample preparation leads mainly to isolated silanol groups on the surface of both silica gel samples. A calorimetric titration was run in cyclohexane at room temperature employing low pyridine concentrations. A heat of 3 kcal mol^{-1} was measured, indicating an interaction with an isolated silanol. The large difference of nearly 20 kcal mol^{-1} in the cyclohexane and gas–solid enthalpy must be associated with the contribution from the nonspecific dispersion interactions of gaseous pyridine with the solid surface in the gas phase–solid equilibrium. When the equilibrium is studied in a cyclohexane solution of pyridine instead of gaseous pyridine, these interactions are canceled out. A cyclohexane molecule on the solid surface of the reactants is displaced by a pyridine molecule in the adduct, roughly canceling the nonspecific dispersion interactions. The nonspecific pyridine–cyclohexane interactions lost by the reactant leaving the solution are replaced by cyclohexane–cyclohexane interactions from the displaced cyclohexane entering solution. These solution interactions correspond to a small fraction of the heat of solution because the pyridine molecules on the surface are interacting with cyclohexane molecules at the interface.

***E* and *C* Analysis.** Enthalpy values for a series of different donors bonding to silica gel have been measured by a calorimetric procedure using dilute base.[10] The reported enthalpy for the reaction of pyridine with silica gel correlated with that determined by the Cal-Ad method for the most acidic site on silica. As a result, reported values for the enthalpies of adduct formation reported for the other bases can be assumed to involve only the same site and the donors can be assumed to be fully coordinated to the extent of a ±1 kcal mol^{-1} error limit. The *E* and *C* model[24] (eq 6) has been used to interpret enthalpies of reactions in solution to determine when contributions other than donor–acceptor interactions are involved. Accordingly, it was of interest to

$$-\Delta H = E_A E_B + C_A C_B + W \qquad (6)$$

determine if the enthalpies measured calorimetrically for coordination to silica gel were dominated by the same factors that influence bond strengths in solution. The enthalpies and reported[24c] E_B and C_B values for the donors are substituted into eq 6 to produce a series of equations that are solved for E_A and C_A. The E_A and C_A values obtained for the strongest site on silica gel are 2.30 ± 0.88 and 2.48 ± 0.15 (kcal/mol)$^{1/2}$, respectively. This *C*/*E* ratio (1.08) is similar to the *C*/*E* ratio for the hydrogen-bonding acceptor octanol (*C*/*E* = 1.02).

Table II. Results of *E* and *C* Fit for the Most Acidic Site on Silica

base	$-\Delta H_{exp}{}^{a}$ (kcal/mol)	$-\Delta H_{calc}$ (kcal/mol)	deviation (kcal/mol)
acetonitrile	6.2	5.5	0.6
tetrahydrofuran	9.5	9.2	0.3
3-methylpyridine	11.1	(13.3)^{c}	2.2
pyridine	12.6^{b}	12.9	0.3
4-methylpyridine	13.0	13.5	0.5
triethylamine	18.3	17.3	1.1
quinuclidine	18.3	18.5	0.2

[a] All experimental heats were obtained from ref 9 except where otherwise noted. [b] From this paper. [c] Omitted from the fit and calculated with the resulting E_A and C_A parameters.

The data fit is shown in Table II. A good fit results, indicating that the enthalpies for the adsorption of these donors by silica gel are dominated by donor–acceptor interactions. These E_A and C_A values can be combined in eq 6 with the E_B and C_B values reported[24c] for over 70 different donor molecules to predict their enthalpies of adsorption from cyclohexane. The enthalpies of displacement reactions can be calculated from the differences in the enthalpies of adsorption to determine the enthalpic contribution to competitive binding. Several practical applications of competitive binding exist including separations, adhesion, removal of bound molecules, and solvent selection for acid-catalyzed reactions.

Conclusions

Upon evacuation of silica, there is a change in the types of hydroxyl groups available for reaction. With mild pretreatment, thre are a large number of poly-hydrogen-bonded silanols which give rise to the strongest binding. Also present are mono-

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(23) Cardona-Martinez, N.; Dumesic, J. A. *J. Catal.* **1990**, *125*, 427.

(24) (a) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251–277. (b) Drago, R. S.; Ferris, D. C.; Wong, N. *J. Am. Chem. Soc.*, **1990**, *112*, 8953–8961. (c) Drago, R. S.; Vogel, G. C.; Dadmun, A. Submitted for publication.

hydrogen-bonded silanols which are weaker acids than the poly-hydrogen-bonded silanols. A noticeable change in the strength of the two sites occurs upon evacuation at 200 °C. At this point the poly-hydrogen-bonded silanols have been effectively eliminated, leaving the mono-hydrogen-bonded silanol as the strongest site while a new, weaker site has appeared that can be attributed to the isolated silanol on the silica surface. The enthalpies of adsorption of donor molecules by the strongest site are dominated by donor–acceptor interactions. Gas phase–solid equilibria contain substantial contributions to the enthalpy of adsorption from nonspecific, dispersion interactions.

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