Relationship between Differential Heats of Adsorption and Brønsted Acid Strengths of Acidic Zeolites: H-ZSM-5 and H-Mordenite

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Abstract: We have used microcalorimetry to measure the differential heats of adsorption of both a series of alkylamines and a series of substituted pyridines in H-ZSM-5 and H-Mordenite. With few exceptions, the differential heats are approximately constant to coverages close to the expected Brønsted site concentration. Both zeolites show good correlations between the average differential heats of adsorption and the gas-phase proton affinities of the basic adsorbates. Slopes of the correlation lines for the two zeolites are similar; the intercepts differ by about 15 kJ/mol. We use this data set to demonstrate that a self-consistent, quantitative Brønsted acidity scale for solid acids cannot be obtained from heats of adsorption of ammonia or pyridine or any other single reference base. However, the correlation between heats of adsorption and gas-phase proton affinities does provide a useful starting point for a more complete description of the thermochemistry of proton transfer reactions in zeolites. Deviations from the correlation curves for specific zeolite/adsorbate pairs can be used to infer how the strengths of Coulombic, hydrogen-bonding, or van der Waals interactions change with structure of either the zeolite acid or the adsorbate base.

Introduction

Zeolite acid strengths have often been studied using ammonia and/or pyridine titrations. Countless publications purport to use measurements of adsorption or desorption of these bases (e.g. TPD, or IR, or microcalorimetry) to demonstrate either acidity differences between zeolites of different crystal structures or acid strength distributions among available acid sites within a single zeolite.[1] In this paper we demonstrate that the logic behind these approaches to the determination of solid acid strength is inherently flawed. We show that any approach built around interactions with a single basic probe molecule, whether it is ammonia or pyridine or any other base, is unable to generate quantitatively useful insights about acid-catalyzed zeolite chemistry. A more successful approach will require a better understanding of how the free energy of proton transfer is affected by changes in the structure of the base. Starting with ammonia and pyridine as parent structures, we show that heats of adsorption of substituted amines and pyridines in two different zeolites vary in direct proportion to their gas-phase base strengths. In combination with a thermochemical cycle that we have described previously,[2] these measurements can be used to obtain more general insights about how the structures of the base and the zeolite interact to yield potential energy surfaces for proton-transfer reactions.

For this study, we have chosen to compare the zeolites H-ZSM-5 and a dealuminated mordenite, H-M. These zeolites are well-suited for a study of this type, for reasons in addition to their commercial importance. First, both can be prepared as high-silica materials in which Brønsted acid sites are well separated. In principle, this allows one to treat each material as a collection of independent, noninteracting acid sites. Second, the Lewis-acid site concentrations can be controlled. For H-ZSM-5 low Lewis acid site densities result from careful preparation and pretreatment procedures. For mordenite, which is difficult to prepare directly in a high-silica form, it is possible to remove most of the Lewis-acidic nonframework species formed during steam dealumination. Finally, the pore dimensions of these materials are sufficiently different, so that steric effects on binding energies might be observed with suitably sized bases.[3] H-ZSM-5 is a medium-pore material, consisting of interconnecting, 10-membered rings. H-M is a large-pore zeolite, with one-dimensional, 12-membered rings, connected by 8-membered rings.

Experimental Section

The equipment used in the microcalorimetry and the simultaneous temperature-programmed-desorption (TPD) and thermogravimetric-analysis (TGA) measurements is described in other papers.[4,5] The TPD-TGA studies used 10 to 20 mg of sample placed in the pan of a Cahn microbalance. This system was evacuated to $\sim 10^{-7}$ Torr after exposure to several torr of each adsorbate at room temperature. Following evacuation for 1 h, desorption was monitored using the mass change from the microbalance and the signal from a mass spectrometer as the sample was heated at 20 K/min. The microcalorimeter is a home-built, Calvet-type instrument which allows the use of relatively large samples ($\sim$0.5 g) spread into very thin beds ($\sim$1-mm thick) for rapid adsorption and heat transfer. The time required for collecting the heat from a pulse of adsorbate was on the order of 10 min.[6]

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The microcalorimetry measurements were performed between 460 and 480 K.[7] The dosing volume and all tubing leading from this to the sample were also held at the sample temperature to prevent adsorption on the walls. In a typical experiment, the 63-cm³ dosing volume was filled with 1 to 5 Torr of vapor and exposed to the evacuated sample. For coverages below one adsorbate molecule per Brønsted acid site, all of the adsorbate was taken up by the zeolite, as determined by the final pressure above the sample. The performance of the microcalorimeter has been documented in previous publications.[6,7] The measured heats are independent of sample size.[4] For coverages below 1 molecule/Al, the differential heats for ammonia and pyridine have been shown to be the same in various H-ZSM-5 samples, independent of the Si/Al ratio.[7] The data were highly reproducible, although the coverage at which the heats drop varied by as much as ~5% from experiment-to-experiment, mainly due to the precision with which the mass of the dehydrated sample in the calorimeter could be measured.

The H-ZSM-5 sample was received in the Na form from Chemie Uetikon AG (Zeocat-Pentasil-PZ-2/54Na). It was then calcined, ion exchanged with 2 M $(NH_4)_2SO_4$ at 360 K, and heated to 770 K in order to obtain the hydrogen form. Following this pretreatment, it had a porosity of 0.174 cm³/g, determined from the uptake of 14.5 Torr of *n*-hexane at room temperature, compared to the ideal pore volume of 0.19 cm³/g. The Brønsted-acid site concentration, determined from the amount of isopropylamine which decomposed to propene and ammonia between 575 and 650 K in TPD-TGA measurements,[8,9] was 500 μmol/g, compared to a bulk Al content, determined from atomic absorption spectroscopy, of 630 μmol/g. The mordenite sample was obtained in the ammonium form from Conteka. It had been steamed and acid leached to a Si/Al ratio of 15 (1100 μmol/g of Al). The pore volume of this sample, determined using 1.5 Torr of O_2 at 78 K, was 0.183 cm³/g and the Brønsted site density was 800 μmol/g. Other data on these H-ZSM-5 and H-M samples, including microcalorimetric measurements of ammonia and pyridine, have been published.[6]

Both zeolites had previously been examined using ¹³C NMR of adsorbed C-2 ¹³C-labeled 2-propanone.[10] 2-Propanone forms strong hydrogen bonds with the Brønsted sites which result in significant charge transfer (and therefore a large chemical shift) at the central carbon, 16.9 ppm from solid acetone for H-ZSM-5 and 15.1 ppm for H-M. 2-Propanone is even more sensitive to interactions with Lewis sites formed by nonframework Al, where chemical shifts on the order of 25 to 30 ppm are observed.[11] For the two zeolites used in this study, the Lewis-site concentrations determined in this way were ~1% of the Brønsted-site concentration for H-ZSM-5 and ~10% for H-M. Therefore, the sites probed in the adsorption measurements are overwhelmingly Brønsted sites.

TPD-TGA measurements were made for each adsorbate on both samples prior to the microcalorimetry work, in order to determine the adsorption uptakes and stoichiometries and to work out procedures for preparing the adsorbates. The particular adsorption systems that were studied are listed in Table 1. Each of the compounds was obtained from Aldrich Chemical Co. at nominal purities of >98%. Small vials of liquid were further purified by several freeze–thaw cycles before use in calorimetry. Upon exposure to several Torr at room temperature, each zeolite picked up masses >1 molecule/site for each adsorbate, with the exception of 2,6-dimethylpyridine in H-ZSM-5, which took up less than 0.5/site and was not studied further. Following evacuation, the coverages at room temperature varied depending on the particular adsorbate and zeolite; however, in the TPD-TGA curves, the coverage at 450 K was close to 1 molecule/site for each adsorbate on both zeolites. Given the difficulties associated with the interpretation of desorption peak temperatures,[12] particularly for molecules with low diffusivities like amines in zeolites,[13] we have not attempted to interpret the TPD curves further.

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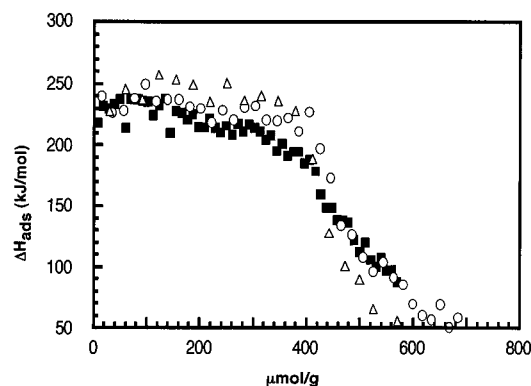
Figure 1. Differential heats of adsorption of 2-methylpyridine (triangles), 4-methylpyridine (circles), and 3-methylpyridine (squares) on H-ZSM-5 at 470 K.
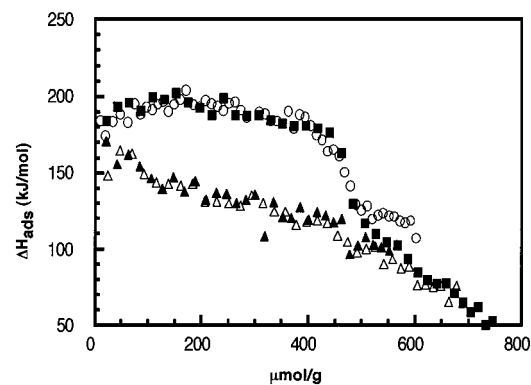

Figure 2. Differential heats of adsorption of 3-fluoropyridine (squares), 3-chloropyridine (circles), and 2-fluoropyridine (triangles, two runs) on H-ZSM-5 at 470 K.
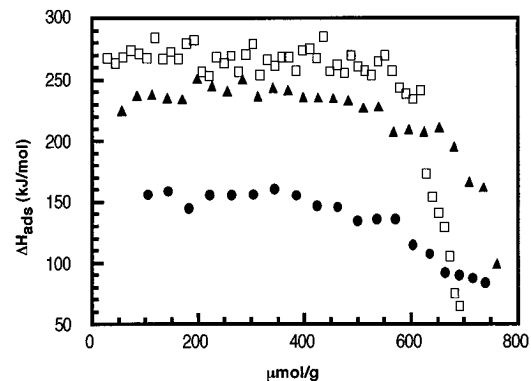

Figure 3. Differential heats of adsorption of 2-fluoropyridine (circles), 2-methylpyridine (triangles), and 2,6-dimethylpyridine (squares) on H-M at 470 K.

Results

Our group has previously published calorimetric data for a range of alkylamines and pyridine in H-ZSM-5[14] and for ammonia and pyridine in H-M.[6] In the present study, we have extended the previous work by measuring heats of adsorption as a function of coverage for several alkylamines in H-M and a series of substituted pyridines in both zeolites. The new data are shown in Figures 1−4 as follows: Figure 1, methylpyridines on H-ZSM-5; Figure 2, halopyridines on H-ZSM-5; Figure 3, variously substituted pyridines on H-M; and Figure 4, alkylamines on H-M. Differential heats of adsorption obtained from these data sets are collected in Table 1 along with all previous

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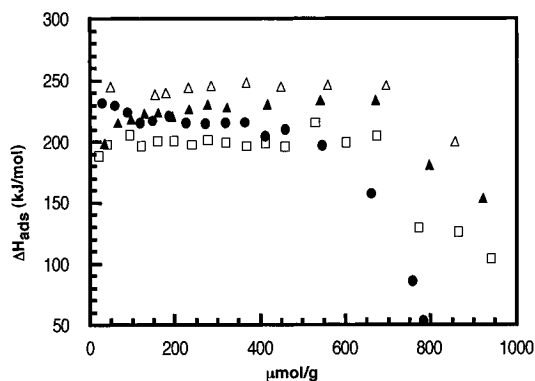
Figure 4. Differential heats of adsorption of methylamine (squares), dimethylamine (closed triangles), trimethylamine (circles), and *n*-butylamine (open triangles) on H-M at 470 K.

Table 1. A Comparison of Adsorption Enthalpies in H-ZSM-5 and H-Mordenite to Gas-Phase and Solution-Phase Basicities

	ΔH (kJ/mol)		PA[d]	$-\Delta H_{prot,s}°$
	(H-ZSM-5)	(H-Mordenite)	(kJ/mol)	(kJ/mol)
pyridine	200 ± 5	200 ± 5	922.2	20.1
2-fluoropyridine	135 ± 13	145 ± 13	886.2	-6.7^c
3-fluoropyridine	190 ± 7		898.7	12.8^c
3-chloropyridine	190 ± 9		902.5	10.9
2-methylpyridine	245 ± 9	235 ± 13	936.0	26.0
3-methylpyridine	225 ± 10		932.2	24.6
4-methylpyridine	230 ± 11		936.0	25.7
2,6-dimethylpyridine		265 ± 11	950.2	30.3
ammonia	145^a	160^b	857.7	52.3
methylamine	185^a	200 ± 7	895.8	55.2
dimethylamine	205^a	225 ± 6	922.6	50.4
trimethylamine	205^a	220 ± 7	938.5	36.9
n-butylamine	220^a	245	916.3	58.5

a Parrillo, D. J.; Gorte, R. J.; Farneth, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 12441. *b* Parrillo, D. J.; Gorte, R. J. *J. Phys. Chem.* **1993**, *97*, 8786. *c* The $-\Delta H_{prot,s}°$ was calculated by assuming $T\Delta S \sim 1$ kcal/mol. *d* Ave, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 2, p 1.

results. The differential heats and uncertainty levels reported in Table 1 were determined by taking the average and standard deviation of all the points below a coverage of 400 μmol/g for H-ZSM-5 and below 600 μmol/g in H-M. For many of these adsorbates, the binding energies are quite large. This strong interaction restricts the ability of adsorbate molecules to migrate to the "strongest" sites, even at 473 K. As a result, we believe that attempts to extract site distributions (if sites of different strength really exist) from the coverage-dependences of Figures 1−4 are not justifiable.[1b,7,15]

These are the first reported calorimetric measurements for a number of these adsorbates. However, there are several previous reports for the parent species, ammonia and pyridine, in both H-M and H-ZSM-5, and one report that compares the complete methylamine sequence in these two zeolites.[16] The calorimetrically determined binding energies of ammonia and pyridine vary over a wide range.[1b,17] It seems likely that the variations result from differences in the samples themselves, their pretreatment, and the methods used to perform the calorimetry. The numbers that we report for ammonia and pyridine in Table

(15) Some of these adsorbates probably bind to the zeolite under kinetic control and some under thermodynamic control at these experimental conditions, and yet all show similar, essentially constant, coverage dependence. We believe this observation is probably best interpreted as implying constant site strength.

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1 lie near the mean of reported data and we believe that they are representative of binding at non-interacting Brønsted acid sites in carefully prepared crystallites of these zeolites. For example, we have obtained the same values for samples of H-ZSM-5 from very different preparations.[7] However, our main concern in this work is not the absolute values of the calorimetric binding energies, but rather the relative heats of adsorption within a series of structurally related bases. From this point of view, the internal consistency of the data set is important.

(1) As shown in Figures 1−4 and in previous papers,[6,7,14] nearly all of the adsorbates collected in Table 1 show constant differential heats of adsorption out to a coverage that is close to what is predicted for the Brønsted site density from the isopropylamine titrations. In only one case, 2-fluoropyridine (Figure 2), is the deviation of any single differential heat pulse greater than $\pm 10\%$ of the mean value over the range from zero coverage to Brønsted site saturation.

(2) The falloff in the differential heats at Brønsted site saturation is generally well-defined and occurs at the same coverage $\pm 10\%$ from adsorbate to adsorbate.

(3) There is an excellent overall correlation between heats of adsorption and gas-phase proton affinities of adsorbed bases for both zeolites (vide infra). This observation would be hard to rationalize unless the differential heats are dominated by proton transfer energetics. For the methylamines, Dumesic et al. have also reported this correlation.[16] Their work is qualitatively similar to this study in several respects, for example, a clear correlation between average differential heats and proton affinities, a large negative deviation from the correlation for trimethylamine, and generally higher values for adsorption of a given base on H-M than H-ZSM-5. However, there are significant quantitative differences between the two calorimetric data sets that are not understood.

We have chosen to examine binding of substituted pyridines because the proton affinities vary significantly both with the nature and the ring position of the substituent within this series. These differences in base strength are reflected in the observed heats of adsorption in Figures 1−3. The methylpyridines are all stronger gas-phase bases than pyridine itself. In agreement with this, each of the methylpyridines adsorbs more strongly than the parent, exhibiting heats of adsorption of 245, 230, and 225 kJ/mol for the 2-, 3- and 4-methyl-substituted pyridines in H-ZSM-5 (Figure 1). The averaged heats of adsorption of the 3- and 4-methylpyridines are probably not significantly different. However, the higher heat of adsorption of 2-methylpyridine is well outside the measurement error. This may imply that a methyl group at the 2-position can provide additional binding energy through enhanced van der Waals interactions with the lattice. Clearly, the 2-methyl group does not hinder the molecule from approaching the zeolite acid site to within proton transfer distance.

The halopyridines are all weaker gas-phase bases than pyridine itself. 3-Chloro- and 3-fluoropyridine have differential heats of 190 kJ/mol; but 2-fluoropyridine exhibits a heat which is much lower, ~135 kJ/mol. The 2-fluoropyridine calorimetry is also unusual in showing continuously decreasing binding energies with coverage. The usual drop in the differential heat at the Brønsted site saturation coverage is not clearly resolved. The 2-fluoropyridine experiments were repeated with a larger sample and with additional purification of the liquid to be certain that these differences from more typical behavior are not artifacts of the dosing procedure. Since the differential heats appear to decrease with coverage, it might be more meaningful to compare the initial rather than the average heats of adsorption of the halosubstituted pyridines. Even so, the initial heat of adsorption

of 2-fluoropyridine, ~150 kJ/mol, is considerably lower than that found for chlorine or fluorine at the 3-position. Therefore, as with the methyl-substituted pyridines, substituents in the 2-position seem to have an especially large influence on the proton transfer binding energy in H-ZSM-5.

Figure 3 is a plot of representative pyridines in H-M. For pyridine itself, 2-methylpyridine, and 2-fluoropyridine, the differential heats of adsorption are 200, 235, and 145 kJ/mol, respectively, reasonably close to the values observed on H-ZSM-5. Because of the larger pore dimensions of H-M, it was also possible to adsorb 2,6-dimethylpyridine, a molecule that is too large to fit into H-ZSM-5 pores. 2,6-Dimethylpyridine is a much stronger gas-phase base than monomethyl pyridines, significantly extending the range of proton affinities which have been examined. For 2,6-dimethylpyridine, the average differential heat was 265 kJ/mol, 65 kJ/mol higher than that observed for pyridine in H-M. The presence of methyl groups on both sides of the nitrogen does not prevent proton transfer, and in fact, additional stabilizing interactions with the lattice are implied by the high binding energy.

Figure 4 gives data for the series of alkylamines methylamine, dimethylamine, trimethylamine, and *n*-butylamine in H-M. 2-Propylamine in H-M has been reported previously.[6] We have also previously reported on the adsorption of this series in H-ZSM-5.[14] Average differential heats of adsorption for methylamine, dimethylamine, trimethylamine, 2-propylamine, and *n*-butylamine were 200, 225, 220, 220, and 245 kJ/mol, respectively, in H-M, compared to values of 185, 205, 205, 205, and 220 kJ/mol, respectively, in H-ZSM-5. The differential heats of adsorption for each of the alkylamines is 15 to 20 kJ/mol greater in H-M than in H-ZSM-5. This is also the difference observed for ammonia (Table 1), where the differential heats were 145 and 160 kJ/mol in H-ZSM-5[7] and H-M.[6]

Discussion

I. Scales of Brønsted Acidity for Solid Acids. Any useful scale of Brønsted acid strength must be able to predict variations in proton transfer equilibrium constants as the base strength of the adsorbate is changed. For example, a scale that declares AH to be a stronger acid than A′H based on measurements of proton transfer to ammonia is only useful if it can then be used to predict the relative degrees of protonation of hexane, or benzene, or other reagents of importance in zeolite-initiated catalytic chemistry. Our data demonstrate that two of the most common methods for ranking zeolite acid strengths are unable to be used this way, and therefore can have only very limited predictive capability.

Hammett H_0 Values. Ammonia is a stronger base than pyridine by approximately 20 kJ/mol at 300 K in water. The pK_a of ammonium ion is 9.2; that of pyridinium ion is 5.2.[18] On the other hand, in the gas phase, pyridine (proton affinity = 924 kJ/mol) is a stronger Brønsted base than ammonia (proton affinity = 854 kJ/mol) by 70 kJ/mol.[19] For both zeolites that we have examined, H-ZSM-5 and H-mordenite, pyridine acts like a stronger base than ammonia. That is, the binding energies of these two classic titrants for solid Brønsted acids reflect their relative gas-phase basicities, **not** their relative pK_as. This observation has been made by other investigators with other
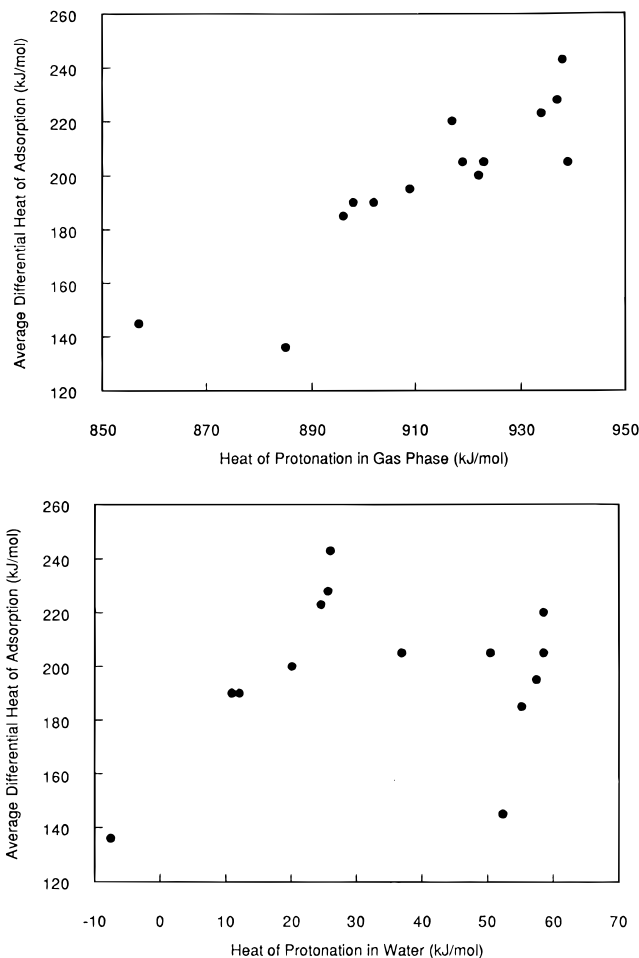

Figure 5. (Top) Differential heats of adsorption of amines and pyridines on H-ZSM-5 at 470 K vs gas-phase proton affinities. (Bottom) Differential heats of adsorption of amines and pyridines on H-ZSM-5 at 470K vs aqueous heats of protonation.

zeolites as well.[8,20] In fact, as shown in Table 1, and for H-ZSM-5, in Figure 5, we observe a much better correlation of binding energies with gas-phase basicities than with aqueous basicities—not just for the parent structures, ammonia and pyridine, but over the whole range of substituted amines and pyridines that we have examined.

These observations clearly call into question the use of the pK_a scale to rationalize proton transfer reactions to adsorbates in zeolites. Hammett H_0 values are an extension of the aqueous pK_a scale. Hammett H_0 values are assigned to solid acids based on apparent equilibrium constants for proton transfer to a set of reference bases of known pK_a, nitroaromatics, for example. A Hammett H_0 value is then intended to be used to predict, or at least rationalize, proton transfer equilibrium constants to other, perhaps chemically more interesting adsorbates. Many of the inherent problems with this approach to ranking solid acid strengths have been discussed in previous work,[21] and yet it continues to be widely used to correlate structure/reactivity data for solid acids, largely because of the absence of more reliable alternatives. However, the clear implication of Figure 5 is that one **cannot** expect H_0 values assigned using a set of standard reference bases to predict the relative binding energies of any other bases of significantly different structure, including alkanes,

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alkenes, alcohols, amines, or any of the other classes of reagent molecules that are important for commercial zeolite-initiated chemistry. For example, an H_0 value assigned based onequilibria with alkylamines would seriously underestimate the binding energies of all of the pyridines.

This problem is well-recognized in solution-phase studies, and different extended acidity scales, H_A, H_R, etc., in addition to H_0, have been promulgated for different classes of probe bases.[22] The same approach could be taken to the zeolite data set. However, as Figure 5 suggests, a better alternative, one that leads to more physical insight into the structural factors that influence reactions catalyzed by solid acids, and one that is now within reach through a combination of experimental and theoretical tools, is to use gas-phase proton affinities as a reference condition. Unfortunately, our impressions of the absolute acidities of solid acids have already been seriously distorted by reliance on the H_0 formalism. For example, a solid acid that can protonate nitrobenzene (PA 810 kJ/mol, $pK_a = -11$), and assigned an H_0 value < -11 based on that observation, would not be a strong enough acid to protonate ethanol (PA 794, $pK_a = -2$), methyl mercaptan (PA 788, $pK_a = -7$), or water (PA 723, $pK_a = -1.7$) based on gas-phase proton affinity values.

Ammonia TPD or Microcalorimetry. It is equally fruitless to try to generate a comprehensive scale of relative acidities of zeolites from adsorption enthalpies (measured either directly by microcalorimetry or indirectly by TPD e.g.) using any **single** reference base. Table 1 clearly illustrates the problem. If we were to choose pyridine as the reference base, we would conclude that H-ZSM-5 and H-M have identical average Brønsted acid strengths since they show identical binding energies. On the other hand, using ammonia as a reference base, H-M appears to be the stronger acid because of the 15 kJ/mol greater binding energy. Finally, if we were to choose 2-methylpyridine as the reference base, we would conclude that H-ZSM-5 is the stronger acid based on the 10 kJ/mol higher binding energy for this base.

The reasons that relative acid strengths can depend on the choice of base have been discussed in the large body of work comparing gas-phase and solution-phase proton transfer equilibria.[23] Acids and bases involved in proton transfer reactions interact with the medium in which the proton transfer reaction is carried out by way of specific chemical interactions. In solution-phase proton transfer reactions, the energy differences associated with these interactions as the structure of the acid **or** base is changed are often as large as or larger than the energy differences associated with the proton transfer itself.[24] In the proton transfer reactions that we are investigating, the zeolite serves as both the proton donor and the "solvent" medium. Thus as the base changes, it is not the proton donor strength of the zeolite that changes but rather the specific interactions in the ion pair created by proton transfer. It is only by separating the proton transfer thermochemistry from the ion-pair stabilization thermochemistry that we can hope to understand the intrinsic acidities of different solid acids, and move beyond qualitative comparisons of acidity to a system that has some predictive power.

We have laid out the formalism for doing this in several previous publications.[2,14] It is based on the thermochemical cycle in Scheme 1.

The binding energy of a given base, $\Delta H_{binding}$(1), may be

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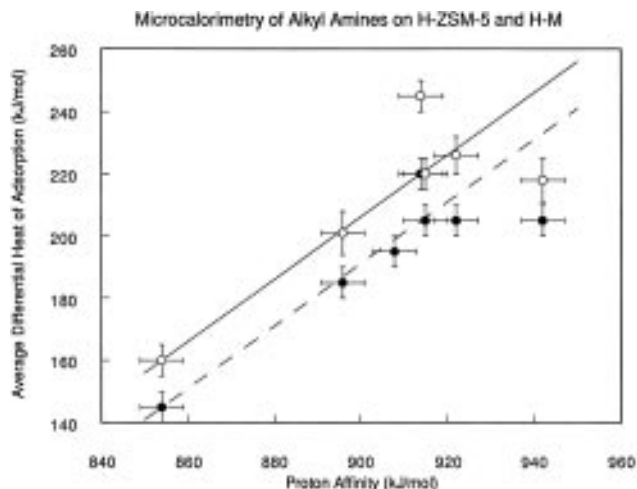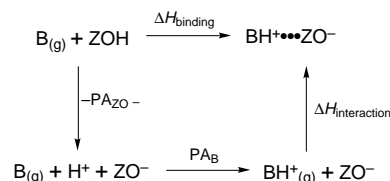(24) Jones, F. M.; Arnett, E. M. *Prog. Phys. Org. Chem.* **1974**, *11*, 263.

Figure 6. Average differential heats of adsorption for alklylamines in H-ZSM-5 (closed symbols) and H-M (open symbols) vs corresponding gas-phase proton affinities.

Scheme 1

imagined as a sum of a hypothetical gas-phase zeolite proton affinity, $PA_{ZO}-$(2), a known gas-phase adsorbate proton affinity, PA_B(3), and an interaction energy associated with the formation of the equilibrium ion pair structure from the hypothetical separated cation and anion, $\Delta H_{interaction}$(4). Unfortunately, there is no direct experimental method for determining the zeolite proton affinity independent of the ion pair interaction energy. Applying this formalism, therefore, requires not only the measurement of binding energies, but also some additional method of estimating one or the other vertical leg. Theoretical methods are well-suited to this approach, and proton affinities of H-ZSM-5 have been calculated by several groups. Values ranging from 1100 to 1600 kJ/mol have been reported.[25] From a purely experimental point of view, some insight into how these two terms contribute to the overall binding can be obtained from measuring the binding energies of structurally related series of bases. This is an experimental approach with a strong pedigree in solution phase acid/base studies, where protonation of the substituted pyridines has been thoroughly analyzed.[26]

II. Structural Series in Gas Phase, H-ZSM-5, and H-M. Figure 6 is a plot of average differential heats of adsorption for alkylamines in H-ZSM-5 (closed symbols) and H-M (open symbols) vs corresponding gas-phase proton affinities. The lines are drawn with a slope of 1 passing through the value for the parent structure, ammonia. Four of the 6 points for H-M fall within experimental error of the line. Four of the 7 points for H-ZSM-5 fall within error limits of the line. The points that deviate for H-M are trimethylamine and *n*-butylamine. The heat

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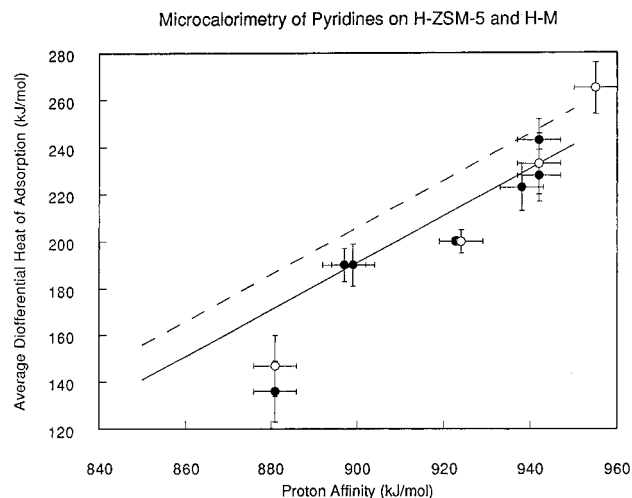
Figure 7. Average differential heats of adsorption of substituted pyridines in H-ZSM-5 (closed symbols) and H-M (open symbols) vs corresponding gas-phase proton affinities.

of adsorption of trimethylamine is about 30 kJ/mol smaller than would be expected from the correlation line. The heat of adsorption of *n*-butylamine is about 25 kJ/mol larger. The points which deviate for H-ZSM-5 are again *n*-butylamine, which has an enthalpy of binding roughly 15 kJ/mol larger than expected, and trimethylamine, which as in H-M falls about 30 kJ/mol below the expectation from the slope of 1. Dimethylamine also falls slightly below the correlation line.

Figure 7 is a similar plot for substituted pyridines. The lines are the same correlation lines that were used in Figure 6, that is slope = 1, passing through the point for ammonia. There is more scatter in this plot. Nevertheless, four of the seven bases fall within error limits of the line for H-ZSM-5. Negative deviations are observed for pyridine itself (15 kJ/mol) and for 2-fluoropyridine (36 kJ/mol). A positive deviation is observed for 2-methylpyridine (10 kJ/mol). On H-M all of the pyridines deviate from the line (although to be fair we have not yet measured the binding energies of 3 of the 4 that correlate in H-ZSM-5). Negative deviations of 15, 30, and 40 kJ/mol are observed for 2-methylpyridine, pyridine itself, and 2-fluoro-pyridine, respectively. A positive deviation of 4 kJ/mol is observed for 2,6-dimethylpyridine.

Another way to think about Figures 6 and 7 is that they are plots of leg 1 vs leg 3 from Scheme 1 for two different series of structurally similar bases. For a given zeolite the proton affinity (leg 2 of Scheme 1) is a constant. Therefore a slope of 1 in these figures implies that the ion-pair binding energy (leg 4 of Scheme 1) also has a constant value, independent of the structure of the base. The intercept of this plot is the sum of these two constants, the two vertical legs of the cycle, the zeolite proton affinity + the ion pair binding energy. For H-ZSM-5 this value is 713 kJ/mol. For H-M this value is 698 kJ/mol. These numbers should be very useful yardsticks for calibrating theoretical modeling approaches to proton-catalyzed reactions in zeolites.

It is remarkable that the slope = 1 line correlates the data so well for both zeolites. The correlation is especially good for the alkylamine series in Figure 6. By drawing the correlation line from ammonia as a reference base, we have implicitly specified the "standard" thermochemical contributions to the ion-pair binding energy as being those that are operative in ammonium cation/zeolite anion pair. Several groups have looked at this ion pair structure using calculational approaches recently.[27] It seems to be generally agreed that the minimum energy structures involve at least bidentate H-bonding of the

ammonium ion to the anionic zeolite lattice. If we take the proton affinity of H-ZSM-5 to be 1300 kJ/mol, as representative of the range of suggested values, then an intercept of 700 kJ/mol implies that the ion pair binding energy is on the order of 600 kJ/mol. A simple Coulomb interaction of two point charges held at 2.7 Å (the equilibrium separation between ZO$^-$ and NH$_4^+$ calculated by Van Santen et al.[17]) in vacuum would be worth 512 kJ/mol. Additional stabilization or destabilization may come from hydrogen-bonding, ion-dipole, or dispersion interactions. The binding energies suggest that these supplementary interactions are worth roughly 100 kJ/mol within this crude model. The whole picture seems reasonably self-consistent.

Let us assume therefore that the binding energy of ammonium ion to the deprotonated ZSM-5 anion is made up of two terms, a short-range Coulomb interaction, and bidentate H-bonding. As we have argued previously,[14] then the simplest interpretation of Figure 6 is that these same contributions are present in equal magnitude for all of the small alkylamines in H-ZSM-5. Since the magnitude of the Coulomb term depends on only the ion separation distance, this implies that the alkylammonium cations can be represented as point charges that sit an equal distance from the lattice anion. The deviations of trimethylamine and *n*-butylamine are best understood as the result of (1) the loss of one H-bond in the former (relative to ammonium), worth 30 kJ/mol, and (2) the reaching of a critical size or conformational flexibility in the latter so that dispersion interactions between the alkyl side chain and the zeolite walls become possible within the structure optimized for Coulomb interaction. For mordenite, the magnitude of the individual enthalpy contributions from Coulombic and H-bonding interactions might be slightly different to give the different intercept, but the basic picture seems adequate to understand the binding energy/proton affinity correlation in this material as well. Note especially the essentially indentical deviation from the curve for trimethyl-amine in H-M. The slightly larger deviation of *n*-butylamine in H-M may be related to greater conformational freedom available to the alkyl side chain in this larger pore zeolite.

For the pyridinium series the correlation of the binding energies with the slope = 1 line based on ammonium is not as good. Of course pyridinium is a much larger adsorbate than ammonium; it is conformationally rigid, and has only a single proton available for H-bonding. If we assume that there is a comparable correlation line for a monodentate binding of a cationic adsorbate and take trimethylamine as a "standard" for this set of bases we generate Figures 8 and 9. We now have two parallel correlation lines representing bidentate and mono-dentate H-bonding. There is some precedent for this type of approach. In solution, it has been demonstrated that there is a more or less standard contribution to the solvation energy per hydrogen bond for alkylammonium cations.[28]

For H-M, (Figure 9) pyridine itself falls on the line. On the other hand, the larger and more polarizable 2-methyl and 2,6-dimethyl fall above the line like *n*-butylamine in the alkyl series. 2-F falls well below the line presumably as the result of destabilizing interactions between the C–F dipole and the anionic lattice. We might expect these types of interactions to be especially severe in the 2-substitued series where the local dipole should be directed toward the anionic channel walls in the preferred ion-pair geometry. For H-ZSM-5 (Figure 8) the parent pyridine lies above the line based on trimethylamine. But H-ZSM-5 is a medium pore zeolite, and pyridine may be

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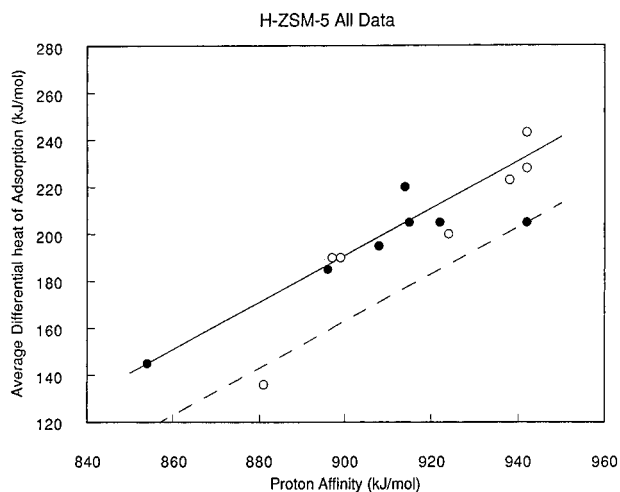
Figure 8. Average differential heats of adsorption of all alkylamines (closed symbols) and pyridines (open symbols) in H-ZSM-5 at 470 K vs proton affinities: solid line drawn with slope = 1 through point for ammonia, dashed line drawn with slope = 1 through point for trimethylamine.
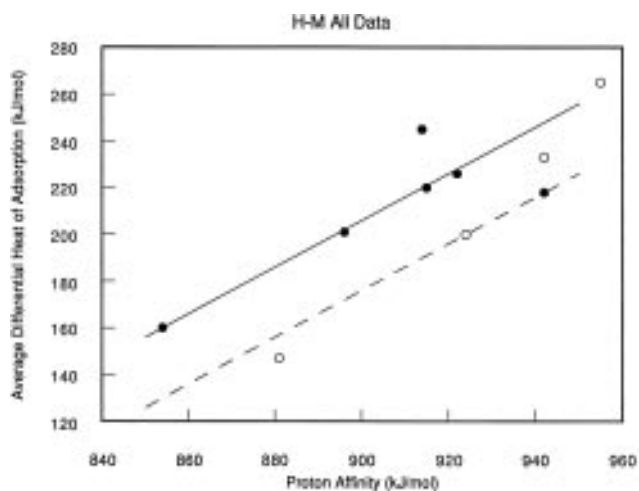

Figure 9. Average differential heats of adsorption of all alkylamines (closed symbols) and pyridines (open symbols) in H-M at 470 K vs proton affinities; solid line drawn with slope = 1 through point for ammonia; dashed line drawn with slope = 1 through point for trimethylamine.

large enough to have significant and slightly favorable short-range secondary interactions that are negligible with the large pore H-M.

Other observations that are consistent with this general picture are the following: (1) The incremental deviation of 2-fluoro-pyridine from the correlation line is the same for the two zeolites. (2) All of the substituted pyridines show larger positive deviations than the parent in H-ZSM-5, as might be expected for short range polarizability-related interactions. (3) The incremental deviations of 2-Me and 2-F from the parent are both greater in H-ZSM-5 than in H-M consistent with the pore

size arguments. (4) The magnitudes of these short range supplemental interaction terms, which range from 15 kJ/mol for *n*-butylamine in H-ZSM-5 to 40 kJ/mol for 2-methylpyridine in H-ZSM-5 and 2,6-dimethylpyridine in H-M, seem to be reasonable in magnitude. The binding energy of propane in silicalite, for example, is 40 kJ/mol.[29] The magnitude of the enthalpy will depend on the polarizability of the adsorbate, and would be expected to fall relative to the alkane model because the adsorbate in the alkyl ammonium ion pair cannot exercise complete translational freedom to optimize the dispersion interaction. The order of magnitude seems right, however.

The data in Figure 6 show that there is a systematic quantitative difference between H-M and H-ZSM-5. From these data alone we cannot say whether that difference is in the proton affinity, the ion pair binding energy, or both. It is likely that there are systematic differences in both. For example, we have shown that there are probably differences in both the proton affinity and the ion pair binding energies in the series H-Al, Ga, and Fe ZSM-5.[30] The structural features that lead to differences in proton affinity may also yield differences in affinity toward other cations. Making the zeolite a stronger acid makes the deprotonated zeolite a weaker base and hence decreases the Coulombic contribution to the ion pair binding energy. The net effect is a tempering of the PA differences in the overall binding energy. But of course for understanding catalysis it is the binding energy (leg 1) (not the proton transfer energy (leg 2 + 3)) that describes the reaction potential energy surface. What this work shows is that, beginning with the proton affinity of the adsorbate, it should be possible to predict binding energies using correlation curves of the type shown here. This can be done without having a direct measure of the "intrinsic acid strength" of the zeolite.

Conclusion

There is a strong correlation between gas-phase proton affinities and differential heats of adsorption of amine and pyridine bases in the zeolites H-ZSM-5 and H-Mordenite. There is no useful correlation between aqueous base strengths and differential heats of adsorption. This contrast implies that a Hammett H_0 value is probably not a meaningful description of zeolite acid strength. The data also suggest that a predictive scale of solid acid strength cannot be built from comparative binding energy measurements using any single reference base, like ammonia, since interactions that are specific to individual zeolite/base pairs appear in some cases to have a large influence on the equilibrium constants for proton transfer. The proton affinity correlation provides a useful starting point for understanding the nature of these specific interactions.

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