A Calorimetric Study of Simple Bases in H-ZSM-5: A Comparison with Gas-Phase and Solution-Phase Acidities

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Abstract: We have used microcalorimetry to measure the differential heats of adsorption for a series of simple amines in H-ZSM-5 as a function of coverage. For each molecule studied, the heats of adsorption were approximately constant to a coverage of close to 1 per Al. The average heats of adsorption in the low coverage regime were as follows: ammonia (145 kJ/mol), methylamine (185 kJ/mol), ethylamine (195 kJ/mol), isopropylamine (205 kJ/mol), *n*-butylamine (220 kJ/mol), dimethylamine (205 kJ/mol), and trimethylamine (205 kJ/mol). An excellent correlation is found between these heats and gas-phase, proton affinities. The heats of adsorption increase in increments that are identical to the gas-phase, proton-affinity differences, except for relatively small deviations with trimethylamine and *n*-butylamine. The deviations for trimethylamine and *n*-butylamine imply that there are some interactions between these bound molecules and the zeolite that are specific to those amines. For example, the deviation for trimethylamine could be explained by a decrease in the ability of this molecule to form hydrogen bonds, while the deviation for *n*-butylamine could be due to interactions between the alkyl group and the zeolite walls. In contrast to the excellent correlation between heats of adsorption and gas-phase acidity scales, the correlation with solution-phase acidities is very poor. These results demonstrate the utility of adopting a gas-phase reference condition for understanding the acid–base properties of zeolites.

Introduction

Zeolites are commercially important materials largely because they are strong solid acids. However, placing the concepts of zeolite acidity and acid-catalyzed reactivity onto a firm quantitative foundation remains a key problem in the field.[1] One common practice has been to use a series of Hammett indicators to titrate the acid sites in order to place bounds on the strengths of those sites.[2] This procedure is problematic for a number of reasons.[3] Most important, perhaps, is that the basicities of the reference Hammett bases are established in aqueous media and it is well-known that the relative basicities of a series of bases depends critically on the choice of solvent. The "solvent" effect in typical solid acids is unknown. An indication of how important these solvent effects can be is shown by the interactions between the Brønsted-acid sites in H-ZSM-5 and pyridine or ammonia. The heat of interaction is considerably larger for pyridine than it is for ammonia,[4] even though ammonia is by far the stronger base in water solutions. (The pK_b's for ammonia and pyridine are 4.75 and 8.75, respectively.) Titration by these two bases in a hypothetical, Hammett-indicator study would therefore result in a large discrepancy in the strength of the acid sites in H-ZSM-5.

The most direct method for comparing basicities in zeolites to solution-phase basicities would be to measure equilibrium constants from adsorption isotherms, but this is very difficult in practice. The strong interactions observed for most bases of interest make equilibrium pressures too low to measure or require such high adsorption temperatures for equilibrium to be reached in reasonable times that either the base or the solid acid can decompose. We have chosen to use calorimetric measurements to examine zeolite-base chemistry. Calorimetry provides a direct method for measuring the enthalpies of the acid–base interactions in zeolites. While determination of the entropy of adsorption is also very important for quantifying the acid–base interaction, it seems likely that the main contribution to the adsorption entropies in zeolites will come from a loss in the translational degrees of freedom in going from the gas phase to the adsorbed phase,[5] so that the adsorption entropies may be approximately constant for a series of similar molecules. Therefore, changes in the adsorption enthalpies should dominate the changes in the free energies.

Calorimetry has been used for a number of years to examine the distribution of acid-site strengths in complex zeolitic materials.[6] From our perspective in order to understand the nature of acid–base interactions at the acid sites in zeolites, it is more informative to examine a "simple" material using a series of bases. The ideal, "simple" material for studying zeolite acidity is H-ZSM-5. First, reaction rates for a large number of acid-catalyzed reactions have been shown to increase linearly with Al content.[7] Second, adsorption measurements have shown that well-defined, stoichiometric adsorption complexes can be prepared at the Al sites for simple alcohols,[8-10] amines,[11] thiols,[12] toluene,[13] and acetone.[14] Finally, infrared measurements of the adsorption of pyridine demonstrate that the sites associated with Al are Brønsted-acid

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sites.[11,15] All of this implies that one can view carefully prepared H-ZSM-5 as having discrete, identical, Brønsted-acid sites with a concentration equal to the framework Al content. This is an important simplifying observation in developing a conceptual framework for understanding the factors that control zeolite acid–base chemistry.

We have measured the heats of adsorption of two series of amine bases, methyl-substituted amines (methyl, dimethyl, and trimethylamine) and homologous alkylamines (methyl, ethyl, isopropyl, and *n*-butylamine). Solvent effects are very important for both of these sets of molecules and can even change the ordering of the basicities in each series. Furthermore, the intrinsic basicity of each molecule in the absence of solvent effects is known from the gas-phase proton affinities. In this paper, we will show that the differential heats of adsorption for each of the bases in H-ZSM-5 remain approximately constant up to a coverage of 1 molecule per Al. The adsorption enthalpies change in steps that are quantitatively predicted by the proton affinities of the bases, deviating to a substantial degree only for trimethylamine and *n*-butylamine. The deviation in the heats for trimethylamine and *n*-butylamine begins to define the thermodynamic consequences of other interactions at the binding site.

Experimental Section

The zeolite sample used in this study was provided by Alcoa and had been synthesized in the sodium form without using a template. This particular ZSM-5 sample was chosen because ZSM-5 samples prepared using a template have been shown to have an inhomogeneous Al concentration, whereas materials prepared without a template are homogeneous.[16] The inhomogeneous distribution of Al in template-synthesized materials results in very high Al concentrations near the edge of the crystallites.[16,17] In a previous paper, two of us have shown that inhomogeneities in the Al concentration can lead to a coverage dependence of the differential heats of adsorption, apparently due to molecular interactions between molecules adsorbed at closely spaced, adjacent sites.[18] In contrast, the sites in the material prepared without a template appear to be separated enough so that all the sites are isolated and the heats of adsorption are coverage independent.

Activation of the zeolite was accomplished by ion exchange in 1 M $(NH_4)_2SO_4$, followed by calcination in dry flowing air at 873 K for 1 h. This procedure was repeated twice to ensure that the zeolite contained no residual sodium. The sample appeared to be highly crystalline in X-ray diffraction and showed no amorphous halo, although pore volume measurements using 14.5 Torr of *n*-hexane at 298 K gave a porosity of only 0.124 cm^3/g compared to the ideal value of 0.19 cm^3/g. SEM of the sample indicated that it consisted of crystalline bundles, with individual crystal facets 1 μm in size. The acid-site density of the catalyst was determined using simultaneous temperature programmed desorption-thermogravimetric analysis (TPD-TGA) measurements of isopropylamine. This method of measuring the acid-site concentration depends on the observation that amine molecules adsorbed at a Brønsted-acid site decompose to propene and ammonia in a well-defined feature between 575 and 650 K.[19] The site concentration for this sample was 600 μmol/g, a number which compares favorably with the bulk Al content of 620 μmol/g, determined from atomic absorption spectroscopy.

The adsorption properties of simple amines in H-ZSM-5 had been studied previously.[11] For each of the amines studied, TPD-TGA measurements showed that physically adsorbed molecules, at coverages in excess of 1 per Al, remained in the zeolite up to ~450 K, even in ultrahigh vacuum. At 500 K, each of the molecules was present at a coverage of 1 per Al and infrared measurements demonstrated that the molecules were present at the hydroxyl sites associated with framework Al. From a coverage of 1 per Al, all of the alkylamines except methylamine decomposed completely to olefin products and ammonia at temperatures above 550 K. Methylamine desorbed by a combination of intact desorption and reactive desorption. These observations were very important for determining the conditions for microcalorimetry measurements. Adsorption temperatures in excess of 450 K were necessary to allow mobility of physisorbed molecules and ensure that the Brønsted-acid sites would be populated before other sites began to fill. It was necessary to work below 550 K in order to prevent secondary reactions.

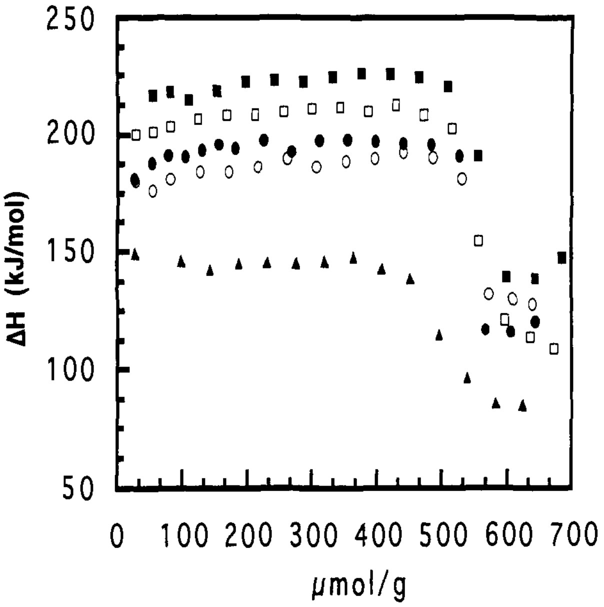

Figure 1. Differential heats of adsorption for alkylamines associated with Al sites in H-ZSM-5. The data are for ammonia (▲), methylamine (○), ethylamine (●), isopropylamine (□), and *n*-butylamine (■).

The microcalorimeter is a Calvet-type, heat-flow calorimeter which was designed and constructed in our laboratory. Details about the apparatus and the experimental procedures have been described elsewhere.[4,18] Approximately 500 to 600 mg of powdered zeolite samples were pressed into wafers and loaded into the cubic sample chamber (2.54 cm on each side), resulting in a bed height of ~1 mm. The samples were heated to 750 K in vacuum before lowering the sample chamber into the system, and the entire system was then equilibrated at 480 K overnight. Gas doses of 10 to 20 μmol were admitted into the sample chamber while the heat flux was monitored from the calorimeter as a function of time. The total heat which evolved in a given pulse was determined by integrating the heat flux with respect to time, using a calibration constant obtained by measuring the heat flux from a Pt wire heated by a known current. The amount of gas which adsorbed during each pulse was determined from the pressure change in a calibrated volume which was held at the adsorption temperature. For coverages below 1 molecule per Al, all of the gas dose adsorbed on the sample, and the equilibrium adsorbate pressure above the sample was below our limits of detection (~10^{-3} Torr) for each of the adsorbates.

Results and Discussion

The differential heats of adsorption as a function of coverage for seven amine bases on H-ZSM-5 are shown in Figures 1 and 2. For each molecule, the heat of adsorption is approximately constant up to coverage above 500 μmol/g, a value approaching the Brønsted-acid site density, 600 μmol/g. At higher coverages the heats drop sharply and a substantial portion of each gas pulse did not adsorb. These results are consistent with a picture of H-ZSM-5 possessing a collection of thermochemically identical, independent binding sites with a concentration of 1 per Al. However, this conclusion is valid only if the adsorbate molecules are mobile enough at the adsorption temperature so that each pulse can interrogate all of the available adsorption sites. If the adsorbate molecules are not mobile (i.e. the adsorbate molecules bind irreversibly at all available sites), then each pulse will sample a kinetically controlled distribution of binding sites and the coverage dependence of the differential heats will reflect the kinetic accessibility rather than the thermochemical stability of the binding sites. For ammonia, at least, we believe that the binding is reversible under these conditions due to the fact that adsorption

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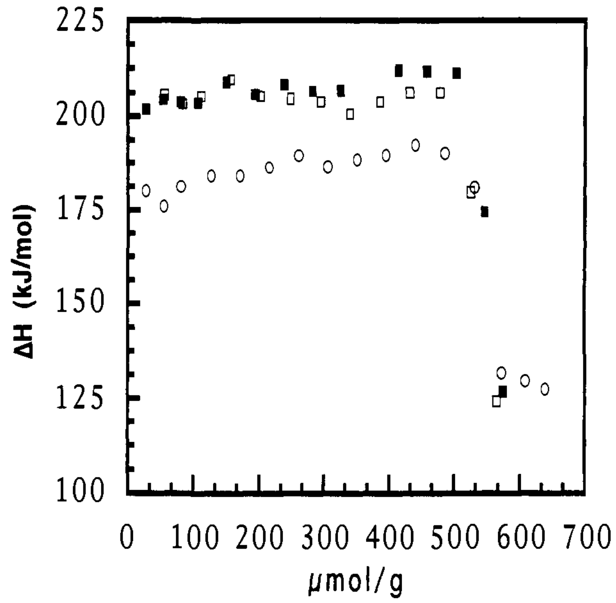

Figure 2. Differential heats of adsorption for methylamines associated with Al sites in H-ZSM-5. The data are for methylamine (○), dimethylamine (■), and trimethylamine (□).

$$\begin{tikzcd}
B_{(g)} + ZOH \arrow[r, "\Delta H_{binding}"] \arrow[d, "-PA_{ZO^-}"] & BH^+ \cdots ZO^- \\
B_{(g)} + H^+ + ZO^- \arrow[r, "PA_B"] & BH^+_{(g)} + ZO^- \arrow[u, "\Delta H_{interaction}"']
\end{tikzcd}$$

Figure 3. Hypothetical, thermochemical cycle used for picturing adsorption at the Al sites in H-ZSM-5.

was carried out near the desorption peak temperature observed in TPD under our conditions.[20] Chemisorbed molecules can probably migrate from site to site much more rapidly than the rate of desorption back to the gas phase in a given crystallite of H-ZSM-5 because some fraction of the adsorption energy would be preserved along the migration pathway. Therefore, the number of sites sampled by ammonia during the integration time is probably large and a thermochemical interpretation of the coverage dependence should be valid.[21] Furthermore, the differential heat of adsorption of ammonia measured in this sample, 145 kJ/mol, is identical to that reported previously for two other H-ZSM-5 samples which had significantly different Al concentrations and had been prepared using a template.[18]

However, for the other molecules, thermodynamic equilibration is less certain. Even if molecules can migrate between sites in a given crystallite, they probably cannot move between crystallites in the sample bed, a process which would require desorption to the gas phase. One can still measure an average differential heat of adsorption for coverages below 1 per Al, but changes with coverage in this regime will be determined in part by kinetics.

The average differential heats of adsorption for coverages below 1 molecule per site measure the enthalpies from formation of the equilibrated ammonium cation/zeolite anion complex for the noninteracting gas-phase amine and the protonated zeolite. This process is represented in step 1 of Figure 3 as $\Delta H_{\text{binding}}$.[8] Table I lists the $\Delta H_{\text{binding}}$ values along with the gas-phase proton affinities and the standard enthalpies of protonation of the amines in water. The gas-phase proton affinities are intrinsic properties of the individual molecules. The enthalpies of protonation in water contain contributions from solvation of both the protonated and free amine by water, in addition to the intrinsic proton-accepting power of the bases. It is interesting to compare the relative heats of formation of the zeolite/amine adsorption complexes with both of these basicity measurements.

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

	ΔH^a (kJ/mol)	PA^b (kJ/mol)	$\Delta H_{\text{prot,s}}{}^{o,c}$ (kJ/mol)
ammonia	145	858.3	52.3
methylamine	185	896.4	55.1
ethylamine	195	909.0	57.4
isopropylamine	205	918.6	58.5
n-butylamine	220	916.9	58.5
dimethylamine	205	923.2	50.4
trimethylamine	205	939.1	36.9

[a] These are average values of the adsorption enthalpies for the molecules at coverages below 1 molecule per Al atom. [b] Values for gas-phase, proton affinities obtained from ref 33. [c] Solution-phase heats of protonation obtained from ref 26.

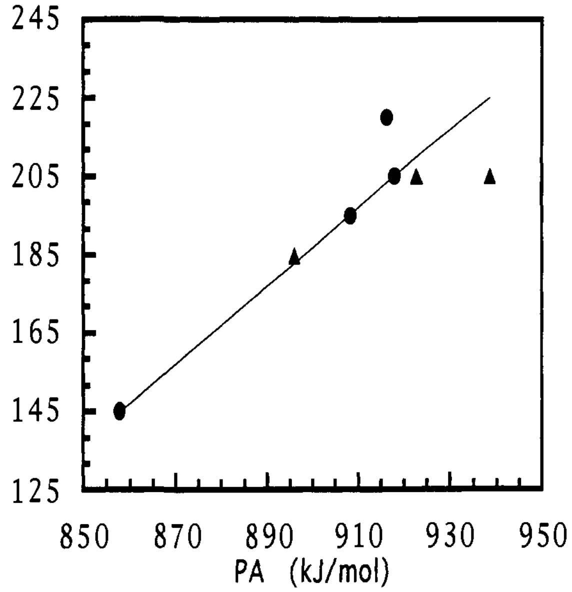

Figure 4. The average differential heats of adsorption for amines in H-ZSM-5 plotted as a function of their gas-phase, proton affinities. The line in the figure has a slope of one and intersects the point for ammonia.

A comparison between the average differential heats of adsorption and the gas-phase proton affinities is shown first in Figure 4. Separate symbols have been used to distinguish the series of methylamines (triangles) and alkylamines (circles). The correlation is excellent. The line shown in the figure was drawn with a slope of one through the point for ammonia. Four of the remaining six molecules fall within 5 kJ/mol of that line. In terms of the thermochemical cycle above, the linear correlation of Figure 4 requires that the sum of the vertical legs of the cycle (i.e. the proton affinity of the zeolite, PA_{zo^-}, step 2, and the intrazeolite ion pairing energy, $\Delta H_{\text{interaction}}$, step 4,) be a constant for this set of bases. From the intercept, we determine the sum to be +712 ± 10 kJ/mol. This number should be extremely useful for calibrating quantum theoretical approaches to understanding zeolite acidity.[22,23]

In fact, the thermochemical analysis can be extended one additional step. PA_{zo^-} is an intrinsic property of the zeolite structure and is independent of the base. Therefore, the linear correlation demonstrated in Figure 4 requires that the intrazeolite ion-pairing energy, step 4 of the cycle, be identical for ammonia,

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methylamine, dimethylamine, ethylamine, and isopropylamine ($\Delta H_{\text{interaction}} = 712$ kJ/mol $-$ PA$_{\text{zo}^-}$). In other words, *the structural changes in the alkyl groups on these bases have no thermochemical influence on the interaction of their corresponding ammonium ions with the zeolite lattice.* The measured differences in the binding energy of these bases in H-ZSM-5 is fully accounted for by the stabilizing effects of the alkyl substituents on the protonated amines in the gas phase. In this light, it is now interesting to consider the two molecules that deviate from the linear correlation.

In the case of *n*-butylamine, the adsorption enthalpy for the 1:1 complex is 15 kJ/mol higher than that which would be predicted by the straight-line relationship between $\Delta H_{\text{binding}}$ and the proton affinity using ammonia as the basis. Since the heat of adsorption of propane in silicalite is 30 kJ/mol,[24] it seems plausible that the additional 15 kJ/mol for *n*-butylamine could be the result of dispersion forces between the alkyl group and the siliceous walls of the zeolite channel. Interactions between the zeolite walls and the alkyl groups in ethylamine and isopropylamine may not be important due to the smaller size of these adsorbates. It may not be possible for the alkyl groups in these complexes to interact effectively with the channels if the binding geometry is optimized to maximize the hydrogen-bonding interaction between the alkylammonium ion and the zeolite conjugate base. In contrast, the *n*-butyl group may extend far enough into the channel volume to regain part of the energy associated with the pure hydrocarbon adsorption in silicalite.

Trimethylamine is the other molecule which showed significant deviation from the line in Figure 4, falling approximately 20 kJ/mol below that predicted by the linear relationship. Dimethylamine also falls slightly below the line and appears to begin the trend. Two possible reasons for the lower than expected adsorption heats are as follows. First, based on *ab initio* calculations of ammonium ion adsorption in zeolites, Teunissen et al. suggested that the formation of two or three hydrogen bonds between the NH_4^+ cation and the zeolite cluster was necessary to stabilize the intrazeolite ion-pair complex.[25] All of the bases we have examined except trimethylamine can form at least two hydrogen bonds to the zeolite matrix. The 20 kJ/mol low binding energy in trimethylamine may be the result of the absence of this second hydrogen bond. An alternative explanation is that ion-size effects could hinder trimethylamine from interacting with the zeolite conjugate base in an optimum manner. While trimethylammonium ions will fit into the channels of ZSM-5, the ability of the ion to orient itself with respect to the zeolite anion may be severely limited relative to the smaller amines. It should be possible to test these explanations by examining other high-silica zeolites with other pore structures.

Figure 5 shows the average differential heats of adsorption plotted as a function of the relative proton transfer energies for the amines in water. The heats of adsorption in H-ZSM-5 are uncorrelated with the aqueous base strengths. In water, the total protonation enthalpies of the amines are dominated by solvation effects, and the relative basicities are controlled by specific solvation differences between the substituted amines, their corresponding alkylammonium ions, and water.[26] Clearly a gas-phase reference condition is a much sounder starting point for understanding zeolite acidity than any approaches that rely on aqueous pK_a values and solvent-filled zeolite pores like Hammett-acidity function correlations. Even in low dielectric constant, non-hydrogen-bonding solvents, the relative amine basicities often do not follow the intrinsic gas-phase order, and specific solvation and ion-pairing effects can lead to complex basicity orders that differ from the intrinsic order.[27]

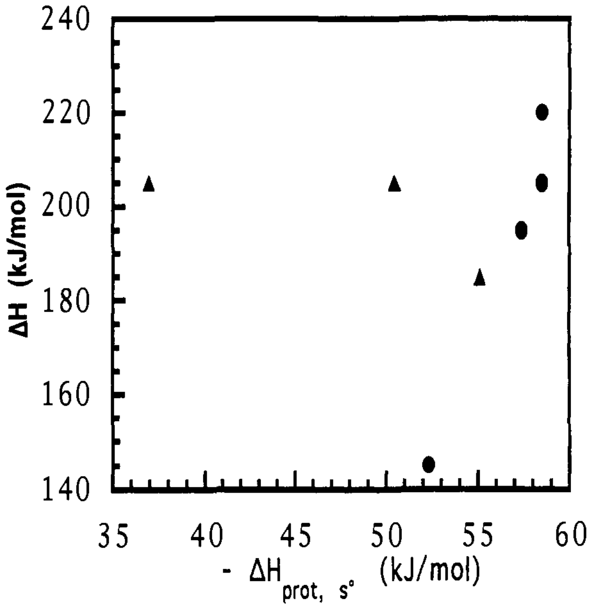

Figure 5. The average differential heats of adsorption for amines in H-ZSM-5 plotted as a function of their proton-transfer energies in water.

Perhaps the most surprising aspect of the strong correlation between the relative gas-phase basicities and the heats of adsorption in H-ZSM-5 is that the slope of the correlation for the alkylamines is one. This implies that the alkyl substituents exert their full intrinsic stabilization effects on the alkylammonium ions that are adsorbed within the zeolite cavities. In solvent systems, it is typical for the protonation enthalpy of a given amine relative to ammonia to be a factor of 3 to 10 lower than the corresponding gas-phase enthalpy difference.[28] For example, Arnett has presented data for a large group of acyclic amines that show a range of gas-phase protonation enthalpies of 121 kJ/mol but only 25 kJ/mol in fluorosulfonic acid and 13 kJ/mol in water. In discussing these data, Arnett declares, "Solvents can interact externally with ammonium ions to cancel the internal effects of charge stabilizing substituents."[29] Apparently within the zeolite, whatever the external interactions are that govern the magnitude of the stabilization enthalpy of alkylammonium ions (presumably some combination of dielectric and site-specific forces), these forces are not sensitive to the alkyl substitution on the nitrogen atom up to sizes approaching the pore diameter.

There *are* cases where slopes of one have been obtained in plots like Figure 4 in solution. It appears that these cases have typically involved large charge-delocalized bases that are not specifically solvated, so that the solvation energies are dominated by ion-dipole or ion-induced dipole forces and, thereby, become insensitive to small structural perturbations.[30] It would be surprising if this were the explanation for the slope of one in Figure 4. There is every reason to believe that, for small charge-localized alkylammonium ions in the oxygen-rich zeolite, site specific hydrogen-bonding forces should be important.[31] Nevertheless, it is known that the hydrogen bond strengths between alkylammonium ions and hydrogen bond acceptors like water are themselves correlated

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with the proton affinities of the corresponding amines.[32] Therefore, if hydrogen bonding of the alkylammonium ions at the zeolite sites *is* important, then for some reason the hydrogen bonds are not responding to changes in the structure of the hydrogen bond donor in the way that equilibrated hydrogen bonds would be expected to.

Determining how and why adsorption enthalpies vary with the structure of the adsorbate is clearly important to understanding reactivity in zeolites. For example, we previously showed that the gas-phase proton affinities could be used to rationalize differences in the TPD results for a series of alcohols—methanol, ethanol, 2-propanol, and 2-methyl-2-propanol—in H-ZSM-5.[8,10] The key feature in the analysis of the alcohol TPD data was estimating the relative energies of oxonium and carbenium ions within the zeolite lattice. Since the gas-phase thermochemistry of these key intermediates is well-known, providing good thermochemical data for $\Delta H_{\text{interaction}}$ was the missing step in establishing an accurate reaction potential-energy surface for acid-catalyzed reactions of the alcohols within zeolite cavities. To carry out the analysis of the alcohol data, we assumed that these interaction energies were independent of structure. In the present work, we have shown that, in fact, the ion pairing interactions *are* independent of structure within a series of structurally similar amines. In the earlier work, we estimated that the sum of the vertical legs of the thermochemical cycle of Figure 3 was 711 kJ/mol using the binding energy of protonated methanol in H-ZSM-5 as the reference point. This estimate is essentially identical to what we have obtained from the current work based on direct calorimetric measurements. The close agreement may be fortuitous since we were uncertain of the exact value of the heat of adsorption for methanol. Nevertheless, it is clear that this thermochemical formalism is equally applicable to non-amine bases in H-ZSM-5 and, with additional calorimetric measurements, will allow detailed information about the nature of the adsorbed intermediates in *reacting* systems to be obtained.

Conclusion

Heats of adsorption for simple amines in H-ZSM-5 scale very well with gas-phase proton affinities but do not scale well with the proton-transfer energies of those bases in water solution. Deviations from a linear relationship between adsorption enthalpies and gas-phase basicities can be explained by secondary interactions between the adsorbate and the zeolite cavity; however, the dominating term in the adsorption enthalpies for amines in H-ZSM-5 is the intrinsic ability of the base to accept a proton.

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