

Calorimetric Study of Alcohol and Nitrile Adsorption Complexes in H-ZSM-5

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Differential heats of adsorption have been measured for a series of alcohols, a series of nitriles, water, and diethyl ether in H-ZSM-5 and silicalite. Higher differential heats in H-ZSM-5 demonstrated that most of the adsorbates had a significant affinity for the Brønsted sites, and the affinity increased with the gas-phase proton affinity of the adsorbate. For the nitriles and diethyl ether, the differential heats were approximately constant up to a coverage of 1/site, after which values fell to the level on silicalite. The heat of formation of the 1:1, stoichiometric adsorption complexes increased with the proton affinity with a slope of 0.37. Heats of formation of stoichiometric adsorption complexes were difficult to identify for water and the alcohols since the differential heats did not fall at a coverage of 1/site. This is evidence for adsorbate clusters, the result of alcohols being both hydrogen-bond acceptors and donors. The implications of these results for understanding zeolite acidity and acid catalysis are discussed.

Introduction

Great strides have been made in the last few years in clarifying the atomic-scale picture of proton-transfer chemistry within zeolite pores. Progress has resulted from a combination of new and better-targeted experimental methods and from the increasing sophistication of theoretical simulation studies. These current models for acid-catalyzed reactions in zeolites focus on the interactions between individual adsorbate molecules and the Brønsted-acid sites associated with the hydroxyls that bridge neighboring framework Si and Al atoms of the zeolite.^{1,2} It has been known for some time that molecules of various kinds chemisorb preferentially at these Brønsted-acid sites and that the resulting localized adsorption complexes have special stability.^{3–8} Adsorption complexes can be prepared at stoichiometric concentrations, that is one adsorbate molecule per Brønsted site, when the zeolite-acid sites are sufficiently isolated. For many materials, like H-ZSM-5 and H-MOR, the concentration of Brønsted sites is approximately equal to the framework Al content,⁹ although this is not the case for all zeolites, such as H-Y, for which certain hydroxyls are inaccessible to adsorbate molecules.¹⁰ Recent work has focused on the determination of the structure and thermochemistry of these complexes.^{11–13} Calculations are also now being used to map out the potential energy surfaces available to these zeolite-acid/adsorbate-base complexes.^{2,14–17}

In two recent papers involving series of alkyl amines and substituted pyridines,^{11,12} we have used microcalorimetry to measure heats of formation of the stoichiometric adsorption complexes. We have analyzed the thermochemical data using methods that are well-established for understanding solvation effects in homogeneous acidic media.^{18,19} In this analysis, heats of protonation for a structurally related series of bases in the medium of interest are compared with intrinsic properties of the bases, these being the gas-phase proton affinities (PA) for proton-transfer reactions. We demonstrated that there was little

correlation between heats of formation of the stoichiometric adsorption complexes (ΔH_{ads}) and the heats of protonation of the same bases in aqueous acids. On the other hand, there was an excellent correlation between ΔH_{ads} and gas-phase proton affinities. As a result, it is clear that a gas-phase reference condition is a much sounder starting point for understanding the kinetics and thermochemistry of acid-catalyzed reactions in zeolites than acidity scales based on solution-phase reference conditions, like $\text{p}K_{\text{a}}$ or Hammett H_0 .

It is important to determine how general this scaling between ΔH_{ads} and PA may be. Proton affinity correlations offer a way to estimate the adsorption equilibrium constants under catalytic conditions.²⁰ In particular, many important, zeolite-catalyzed reactions involve bases significantly weaker than ammonia or pyridine. How useful will proton affinity correlations be for these weaker bases, some of which may not be protonated in the 1:1 adsorption complexes at zeolite-acid sites? Alcohols and nitriles are of special interest. Both have been examined in some detail in spectroscopic and calculational studies. For example, infrared spectra of the adsorption complexes of the simplest members of these series, methanol and acetonitrile, have been interpreted as neutral, hydrogen-bonded structures rather than ion pairs.^{8,21,22} Although there is some disagreement in the literature, most recent calculations have also suggested that the zeolitic proton is not transferred to these adsorbates.^{2,23–25} Furthermore, gas-phase proton affinities are well-established for wide structural variations within both the alcohol and nitrile series.²⁶ We therefore decided to extend our previous work on amines and pyridines by examining the differential heats of adsorption of alcohols, nitriles, and diethyl ether in H-ZSM-5 and by correlating these binding energies with proton affinities.

Experimental Procedure

Two zeolite samples were used in this study. The sample we will call H-ZSM-5 was received in the Na form from Chemie Utikon AG (Zeocat-Pentasil-PZ-2/54Na). It was calcined, ion exchanged with 2 M $(\text{NH}_4)_2\text{SO}_4$ at 360 K, and heated to 770 K

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in order to obtain the hydrogen form. Following this pretreatment, it had a porosity of $0.174 \text{ cm}^3/\text{g}$, determined from the uptake of 14.5-Torr *n*-hexane at room temperature, compared to the ideal pore volume of $0.19 \text{ cm}^3/\text{g}$. The Brønsted-acid site concentration, determined from the amount of isopropylamine that decomposed to propene and ammonia between 575 and 650 K in TPD-TGA measurements,^{5,6} was $500 \text{ } \mu\text{mol/g}$, compared to a bulk Al content, determined from atomic absorption spectroscopy, of $630 \text{ } \mu\text{mol/g}$. Based on ^{13}C NMR of adsorbed acetone, the Lewis-site density appears to be negligible, ~ 5 to $10 \text{ } \mu\text{mol/g}$.²⁷ The sample we will refer to as silicalite was a commercial material (Linde S115) which was kept in the Na form for this work. TPD-TGA measurements with isopropylamine performed on the hydrogen form of this material indicated that the framework Al content was approximately $50 \text{ } \mu\text{mol/g}$.

The microcalorimeter has been described in a previous publication.²⁸ It is a home-built, Calvet-type instrument which allows the use of relatively large samples ($\sim 0.5 \text{ g}$) spread into very thin beds ($\sim 1 \text{ mm}$ thick) for rapid adsorption and heat transfer. The samples were heated in the evacuated calorimeter cell to $\sim 750 \text{ K}$ to clean them before beginning to admit pulses of gaseous adsorbate to the sample. Most of the measurements were carried out at either 350 or 400 K, temperatures that were chosen based on the TPD-TGA results. For the alcohols in particular, TPD-TGA curves show that, following saturation of H-ZSM-5 and evacuation, molecules in excess of 1/site cannot be removed in a reasonable amount of time at room temperature.⁴ Therefore, equilibration of adsorbate molecules to the acid sites requires elevated temperatures in order to collect all of the heat from an adsorbate pulse in the time frame of our experiments. The dosing volume and all tubing leading from this to the sample were also held at the sample temperature to prevent adsorption on the calorimeter walls. In a typical experiment, the 63-cm^3 dosing volume was filled with 1–5 Torr of vapor and exposed to the evacuated sample. For coverages below 1/site, essentially all of the adsorbate was taken up by the zeolite, as determined by the final pressure above the sample. For higher coverages, the pressures above the sample could be substantial. Because the manometer used to measure the pressure could not be heated, the final pressure had to be measured indirectly, by expanding gas from the dosing volume into the manifold that held the manometer. Since adsorption on the walls of the unheated manifold could cause the measured final pressure to be lower than the actual final pressure (and therefore the calculated dose to be larger than the actual dose), especially for the alcohols and water, the differential heats determined at high coverages and on silicalite may, in some cases, be slightly higher than the values shown. In general, the differential heats on H-ZSM-5 and at low coverages should be considered most reliable, since the pressures above the samples were near zero.

Prior to the calorimetric measurements, TPD-TGA measurements were made on each adsorbate in order to determine the optimal conditions for achieving rapid equilibration of the stoichiometric adsorption complexes. The measurements were performed using equipment that has been described previously.^{5,6} Between 10 and 20 mg of sample were placed in the balance pan of a Cahn 2000 microbalance. After heating the sample to 750 K in vacuum, it was exposed briefly to ~ 10 Torr of vapor from the adsorbate of interest for a few minutes and then evacuated for 1 h. The sample temperature was then ramped at 20 K/min while monitoring both the sample weight and the partial pressures of the adsorbate and possible reaction products with a mass spectrometer.

Results

TPD-TGA. TPD-TGA curves for many of the simple alcohols have been published earlier.⁴ In almost every case, a well-defined desorption feature, associated with one molecule per Brønsted site, could be identified. For secondary and tertiary alcohols, this stoichiometric adsorption complex reacted to water and olefin products. The adsorption complex associated with 2-methyl-2-propanol was found to undergo dehydration at room temperature, while water was observed during the desorption of 2-propanol beginning at $\sim 370 \text{ K}$. Initial attempts at calorimetric measurements with these molecules also showed evidence for dehydration at the temperatures needed for equilibration,²⁹ so that no calorimetric results for secondary or tertiary molecules will be reported here.

The primary alcohols, such as methanol and ethanol, exhibited a much lower tendency to undergo dehydration, and their adsorption complexes decomposed, primarily, reversibly back to the alcohol at temperatures higher than that required for dehydration with the secondary and tertiary alcohols. For purposes of our discussion, there are two important points to notice. First, the coverage of alcohol following a saturation exposure and prolonged evacuation was typically close to two molecules per site.⁴ Desorption usually occurred in two distinct features, so that a 1:1 stoichiometric complex could still be identified; however, the TPD-TGA curves did suggest an affinity of more than one molecule with the Brønsted site. Second, the desorption temperatures were rather high considering that these molecules are considered to be weak bases. While desorption peak temperatures are a function of many parameters when the experiments are carried out on a porous catalyst,³⁰ it is still instructive to compare the peak temperatures for methanol and ammonia when the sample and experimental conditions are the same. For desorption with small samples (10–20 mg) in high vacuum (equivalent to essentially infinite carrier-gas flow rate³⁰), the peak temperatures for the reversible decomposition of the 1:1 adsorption complexes back to methanol, ethanol, and ammonia are 410, 440, and 500 K, respectively, from the same zeolite sample.^{4,5} Since the heat of adsorption for ammonia is 145 kJ/mol ^{31,32} and adsorption enthalpies should scale with peak temperature for desorption in a vacuum,³⁰ one can estimate that the heats of adsorption for methanol and ethanol should be roughly 120 and 130 kJ/mol. Differences in the diffusivities of the molecules within the zeolite and adsorption entropies for the two molecules can cause these values to be inaccurate. However, the values are in good agreement with the calorimetric results to be reported shortly and give us confidence in the consistency of our numbers.

The nitriles were found to be quite unreactive under the conditions of our experiments. Adsorption was completely reversible, and only the unreacted nitriles were observed in the TPD curves. Typical of the TPD-TGA results for the nitriles in H-ZSM-5 are those shown for acetonitrile in Figure 1. The initial coverage after even a brief evacuation was very close to $500 \text{ } \mu\text{mol/g}$, or 1 molecule/Brønsted site. All of the acetonitrile desorbed unreacted, as indicated by the peaks present in the fragmentation pattern of the mass spectrum, with a peak desorption temperature of $\sim 420 \text{ K}$. Again, using the same arguments as those for methanol, one can estimate that the heat of adsorption for acetonitrile should be 120 kJ/mol , on the basis of the desorption peak temperatures, again within 10% of the value obtained calorimetrically.

2,2,2-Trifluoroethanol and trichloroacetonitrile were exceptions to the observation of 1:1 stoichiometric adsorption complexes. Both of these molecules adsorbed readily in

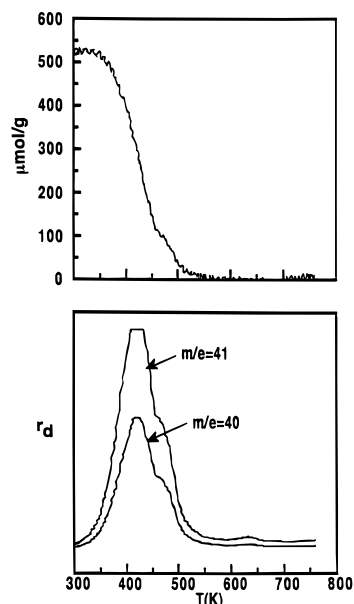


Figure 1. TPD-TGA curves for acetonitrile in H-ZSM-5.

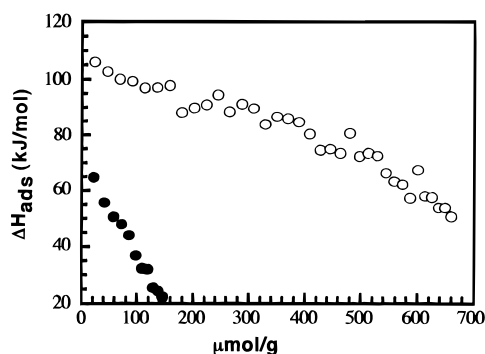


Figure 2. Differential heats of adsorption for water in H-ZSM-5 (○) and silicalite (●).

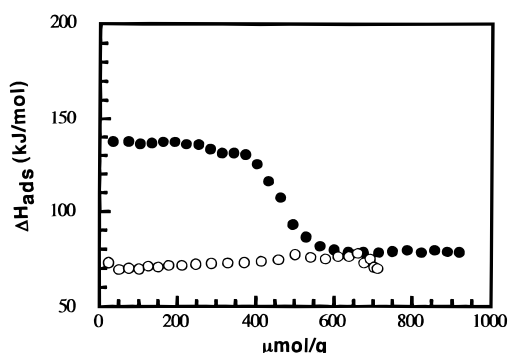


Figure 3. Differential heats of adsorption for diethyl ether in H-ZSM-5 (●) and silicalite (○).

H-ZSM-5 and filled the cavities, but were easily evacuated by pumping at room temperature.

Calorimetric Results. The differential heats for each of the probe molecules that were examined, on both H-ZSM-5 and silicalite, are shown in Figures 2–5. In general, the differential heats were relatively constant on H-ZSM-5, at least at coverages below one molecule per Brønsted site. The average of the differential heats up to a coverage of 400 $\mu\text{mol/g}$, 80% of the Brønsted site density, is therefore defined as the heat of formation for the adsorption complex, with the results tabulated in Table 1. For silicalite, the data in Table 1 were obtained by taking the average between 100 and 400 $\mu\text{mol/g}$, to avoid overemphasizing the effect of defect sites and residual Al sites.

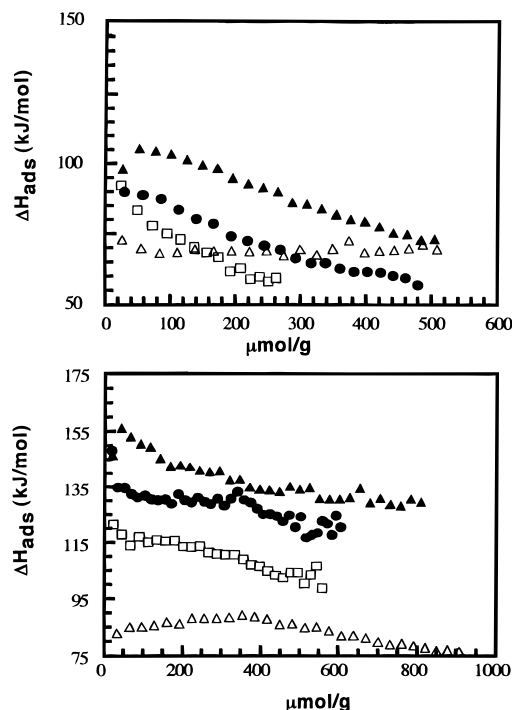


Figure 4. Differential heats of adsorption for trifluoroethanol (Δ), methanol (\square), ethanol (\bullet), and *n*-propanol (\blacktriangle) in (a) silicalite and (b) H-ZSM-5.

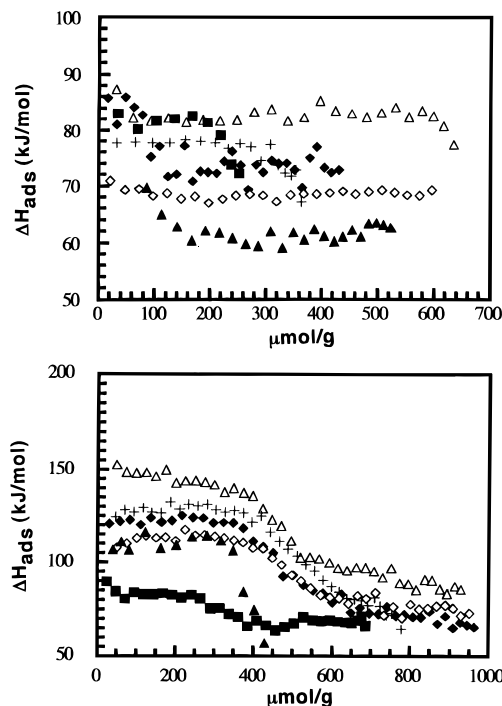


Figure 5. Differential heats of adsorption for acetonitrile (\blacktriangle), propionitrile (\blacklozenge), butyronitrile (Δ), isobutyronitrile ($+$), chloroacetonitrile (\diamond), and trichloroacetonitrile (\blacksquare) in (a) silicalite and (b) H-ZSM-5.

All of the data reported for H-ZSM-5 were obtained at 400 K, with the exception of trifluoroethanol and trichloroacetonitrile, which were measured at 350 K. All of the data on silicalite were measured at 350 K. Differential heats measured at lower temperatures were identical to those reported here at low coverages; however, the heats were not as constant with coverage on H-ZSM-5, and there was other internal evidence from the thermograms that equilibrium was not achieved at the lower temperatures, probably due to chromatographic adsorption in the zeolite crystallites.

TABLE 1: Comparison of Adsorption Enthalpies in H-ZSM-5 and Silicalite to Gas-Phase Basicities

	proton affinity (kJ/mol) ^a	H-ZSM-5 ΔH_{ads} (kJ/mol)	silicalite ΔH_{ads} (kJ/mol)
water	723.8	90 ± 10	30 ± 15
methanol	773.6	115 ± 5	65 ± 10
ethanol	796.2	130 ± 5	70 ± 10
propanol	800.8	145 ± 5	90 ± 10
trifluoroethanol	731.8	90 ± 5	70 ± 5
ethyl ether	838.5	135 ± 5	70 ± 5
acetonitrile	798.7	110 ± 5	60 ± 5
propionitrile	806.7	120 ± 5	75 ± 5
butyronitrile	810.9	145 ± 5	85 ± 5
isobutyronitrile	820.5	130 ± 5	75 ± 5
chloroacetonitrile	773.6	110 ± 5	70 ± 5
trichloroacetonitrile	760.2	75 ± 5	80 ± 5

^a Aue, D. H.; Bowers, M. T. *Gas Phase Ion Chemistry*; Academic Press: New York, 1979; Vol. 2, p 1.

The results for water in both H-ZSM-5 and silicalite, shown in Figure 2, are typical of what is also observed for the alcohols. For silicalite, the heats for water start at ~65 kJ/mol at low coverages, but decrease rapidly at higher coverages. Since the Al content in the sample is 50 $\mu\text{mol/g}$, it is likely that the initial heats may be due to Al, hydroxyl defects, or other impurities. With this taken into account, the results reported are consistent with earlier reports for water in silicalite, ~50 kJ/mol.³³ For H-ZSM-5, the heats start at ~100 kJ/mol and remain at ~80 kJ/mol at a coverage of 400 $\mu\text{mol/g}$. Surprisingly, the heats remain relatively high, even at coverages above 500 $\mu\text{mol/g}$, the Brønsted site density. This is likely due to clustering of water molecules about the Brønsted site. Clustering is known to occur in the gas phase, where neutral molecules tend to cluster around charged species. Evidence for the clustering of four water molecules about each Brønsted site was reported early in studies of adsorption on H-ZSM-5.³⁴ More recently, it was shown that hydronium ions are formed upon adsorption of water in zeolites, but only at relatively high water coverages,^{35,36} again suggesting the clustering of multiple water molecules at the Brønsted sites.

Figure 3 shows results for diethyl ether, which provide an interesting contrast to that for water. On silicalite, the differential heats start at ~70 kJ/mol and increase slightly with coverage. The increase with coverage is due to attractive interactions between diethyl ether molecules and has been observed for a range of other simple molecules in silicalite.³⁷ The absolute value for the differential heat also compares reasonably well with that of *n*-pentane, a molecule of similar size, for which the differential heat in silicalite is reported to be ~65 kJ/mol.³⁸ On H-ZSM-5, the results for diethyl ether are more similar to what we have reported earlier for amines and pyridines.^{11,12} The differential heats begin at ~135 kJ/mol at low coverages and remain essentially constant up to a coverage of 1/site. Above 1/site, the heats fall to the value measured on silicalite. Because the molecule cannot form hydrogen bonds with itself, there is a much lower tendency to form clusters. What makes this data interesting is that, if one assumes that the stoichiometric adsorption complex is formed due to a combination of van der Waals-type interactions and a hydrogen bond with the Brønsted site and that the van der Waals interactions are similar in the complex and for adsorption in silicalite, one estimates the hydrogen bond to be almost 65 kJ/mol, which is a very high value for a neutral, hydrogen-bonded complex.³⁹

Figure 4a shows the differential heats on silicalite for the alcohols that were examined in this study. The heats for trifluoroethanol were essentially constant with coverage, with

a value of 70 kJ/mol. The other alcohols, particularly methanol, exhibited relatively high initial heats, which then decreased at higher coverages. The fact that the heats fall with increasing coverage, rather than rise, suggests defects again contribute to the initial heats.⁴⁰ Therefore, the average values reported in Table 1 are only an upper limit on the true value for alcohols on pure silicalite. The differential heats for each of the alcohols on H-ZSM-5 are shown in Figure 4b. For this sample, the differential heats are nearly constant with coverage, and, as with water, the heats do not fall at coverages above one molecule per Brønsted site, again suggesting the formation of clusters at high coverages. The average differential heats over the first 400 $\mu\text{mol/g}$ for methanol, ethanol, *n*-propanol, and trifluoroethanol were 115, 130, 145, and 85 kJ/mol, respectively. For methanol and ethanol, the agreement with estimates based on TPD peak temperatures, stated earlier in this paper, is excellent.

Data for the nitriles are shown in Figure 5, with results for silicalite in Figure 5a and and results for H-ZSM-5 in Figure 5b. For silicalite, it is likely that interactions with defect sites dominate the initial heats in the first 100 $\mu\text{mol/g}$.⁴¹ The average differential heats at higher coverages probably represent a better measure of the interactions of these molecules with pure silicalite. Because there is less of a tendency of nitriles to form hydrogen-bond networks like in the case for alcohols, the effect of defects is not as long ranging. Neglecting the first 100 $\mu\text{mol/g}$, the average differential heats for acetonitrile, propionitrile, butyronitrile, isobutyronitrile, chloroacetonitrile, and trichloronitrile are 60, 75, 85, 80, 70, and 80 kJ/mol. Because the partial pressures above the sample were significant in the measurements with nitriles on silicalite, there is some uncertainty in the numbers we report; however, the numbers clearly follow the trend that would be expected for alkanes of similar length, with an increase of 10–15 kJ/mol for each CH₂ group on going from acetonitrile to butyronitrile.³⁸ The differential heats are somewhat higher, ~20 kJ/mol, than that for the analogous alkanes, probably due to a stronger interaction with the polar nitrile group.

The nitriles adsorb much more strongly in H-ZSM-5 and exhibit coverage dependences for the differential heats that are similar to that of diethyl ether. The differential heats are relatively constant with coverage over the first 400 $\mu\text{mol/g}$, after which the heats begin to fall to the silicalite value. Taking the average over the first 400 $\mu\text{mol/g}$, the average differential heats for the series of molecules acetonitrile, propionitrile, butyronitrile, isobutyronitrile, chloroacetonitrile, and trichloronitrile are 110, 120, 145, 130, 110, and 75 kJ/mol.

Discussion

Coverage Dependences for ΔH_{ads} . The coverage dependences for the differential heats of adsorption of alcohols and water on H-ZSM-5 (Figures 2 and 4) do not display the special stability of the 1:1 complex stoichiometry that is evident in similar data for nitriles (Figure 5), diethyl ether (Figure 3), or amines and pyridines.^{11,12,31} The differential heats do not drop at a coverage of one molecule per Brønsted site but rather are relatively constant out to stoichiometries that approach two per acid site. The implication is that there are other binding arrangements available to alcohols in H-ZSM-5 that are of comparable stability to the formation of the 1:1 complex at the Brønsted sites.

We may distinguish two possibilities for the nature of the binding interactions at stoichiometries in excess of 1:1. The first possibility is that adsorption occurs in non-hydroxyl-containing regions of the framework rather than at the acid sites and that the energies are still dominated by adsorbate–zeolite

interactions. The second possibility is that adsorption continues to be localized at acid sites and that the energy is strongly influenced by interactions with the first-bound molecule. The binding energies in silicalite serve as a model for the first type of binding. For all the alcohols, differential heats of adsorption in H-ZSM-5 are larger than the corresponding low-coverage binding energies in silicalite. This is true throughout the coverage regime of 0-2 molecules/site. It implies that there continue to be specific adsorbate interactions associated with the presence of acid sites, even beyond the 1 molecule/site stoichiometry. The nitriles offer a nice contrast: (1) For all of the nitriles except trichloroacetonitrile, the observed binding energies above the 1:1 stoichiometry do in fact approach the silicalite numbers. Specific interactions associated with the acid sites apparently occur below the 1:1 stoichiometry but not above it. (2) For trichloroacetonitrile, binding energies in H-ZSM-5 are essentially equal to binding energies in silicalite throughout the coverage range. For this adsorbate, there is apparently no thermochemical preference for interaction with the acidic hydroxyls at stoichiometries in the range of 1:1.

Alcohols, in contrast to nitriles, ethers, and pyridines, can be both hydrogen-bond donors and hydrogen-bond acceptors. This property facilitates the formation of clusters stabilized by extended hydrogen-bond networks. In the gas phase, the stabilization energies of these clusters, dimers, and higher oligomers have been measured. For example, the dissociation energy of a charge-neutral water dimer in the gas phase is only 15–20 kJ/mol. However dissociation of the protonated water dimer, $\text{H}_3\text{O}_2^+ \rightarrow \text{H}_2\text{O} + \text{H}_3\text{O}^+$, requires 125 kJ/mol.⁴² Less extensive data exist for alcohols, but the magnitudes of the dissociation energies are similar. For example, $(\text{CH}_3\text{OH})_2\text{H}^+$ requires 109 kJ/mol for dissociation. Therefore, one might expect that the stabilization energy associated with binding a second water to the first at a zeolite-acid site will be an increasing function of the degree of proton transfer within the 1:1 complex. With only a modest amount of charge separation, a combination of specific interactions with the first adsorbed water and nonspecific interactions with the framework could easily add up to 80 kJ/mol, the average differential heat for H_2O adsorption over the coverage regime that we have examined. For the higher alcohols, the binding energies of the 2:1 complex appear to be larger than for water. They are close to the full, gas-phase-ion, cluster expectation (100–135 kJ/mol). This indicates that there may be more charge separation in the complexes formed by the higher proton affinity alcohols. Indeed, the free energies of formation of the 1:1 and 2:1 complexes cannot be very different for any of the alcohols.

Amines are also capable of both donating and accepting hydrogen bonds; so, by the reasoning that we applied to the alcohols, they should also form stable 2:1 complexes. Both calorimetric and TPD/TGA experiments indicate that they do.^{6,11} However, the amines are all stronger bases than the alcohols. This leads to more stable 1:1 complexes. (The average ΔH_{ads} for $\text{MeNH}_2 = 185$ kJ/mol; for $\text{MeOH} = 115$ kJ/mol.) Furthermore, the gas-phase dimer-dissociation data suggests that the 2:1 complexes of the amines may be less stable than the corresponding alcohols (the dissociation energy for $\text{CH}_3\text{NH}_2\text{--H--H}_2\text{NCH}_3^+ = 91$ kJ/mol; for $\text{CH}_3\text{OH--H--HOCH}_3^+ = 109$ kJ/mol). In any case, the differential calorimetry does resolve the 1:1 and 2:1 complexes for the amines without difficulty. The calorimetry also suggests that, unlike the nitriles, coverages of primary and secondary amines above 1:1 are more strongly bound than would be expected from nonspecific, silicalite-type binding (e.g. 100 kJ/mol for methylamine). In the tertiary amine, trimethylamine, where, like the nitriles, hydrogen-bond

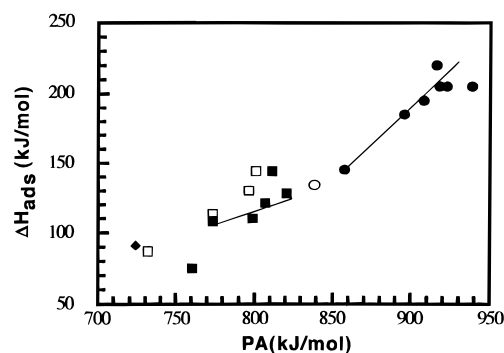
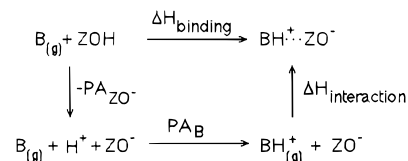


Figure 6. Differential heats of adsorption in H-ZSM-5, from Table 1, plotted as a function of the proton affinity of the various molecules examined. Data for simple alkyl amines (●) were taken from ref 11. The remaining points are for the alcohols (□), nitriles (■), water (◆), and diethyl ether (○).

SCHEME 1



donation is not possible, the differential heats drop rapidly above 1:1 to values below 50 kJ/mol. In the TGA-TPD experiments, it is again not unusual to see stable amine complexes at stoichiometries of 2:1 after pump-out at room temperature.⁶ However, the clear difference in stabilities of the 2:1 and 1:1 complexes shows up in TPD as a large temperature difference between the desorption event corresponding to loss of the second adsorbate molecule (400 K in isopropylamine) and that for the first (600 K in isopropylamine).

Thermochemistry of Neutral and Ion-Pair Complexes.

For ammonia and a variety of other alkylamines, we have shown there is an excellent correlation between the average differential heats of adsorption for the 1:1 complexes in H-ZSM-5 and the corresponding gas-phase proton affinities.¹¹ The data are shown in Figure 6, along with the corresponding data for the alcohols and nitriles. The correlation line for the amines in Figure 6 is drawn with a slope of 1, passing through the point for ammonia. It gives an intercept on the PA axis of 713 kJ/mol, which can be interpreted as a sum of the hypothetical, gas-phase proton affinity of the zeolite and the stabilization energy that results from the interaction of the ammonium ion and the zeolite framework in the ion-pair complex (Scheme 1). Since the zeolite proton affinity is constant, the linear correlation implies that the stabilization energy resulting from interaction of the protonated amine with the deprotonated zeolite is also constant for the set of molecules that falls on the line. This stabilization energy should be made up largely of a Coulombic term and an ionic, hydrogen-bonding term.¹ As the figure shows, significant deviations to higher binding energy for *n*-butylamine and to lower binding energy for trimethylamine are observed. We argued that the lower-than-expected binding energy of trimethylamine was the result of one fewer hydrogen bonds from the cation to the framework in the ion pair and that the higher binding energy for *n*-butylamine was the result of additional interactions between the long alkyl chain and the zeolite walls. This structural and energetic picture was in good agreement with theoretical calculations of the ammonia/H-ZSM-5, 1:1 complex.⁴³

It is interesting to examine the analogous correlations for the more weakly bound alcohols and nitriles. These data are also presented in Figure 6. All of the molecules in these series have

lower proton affinities than ammonia. Furthermore, as mentioned earlier, infrared spectra for methanol and acetonitrile have been interpreted in terms of neutral, hydrogen-bonded structures rather than ion pairs. Nevertheless, there is clearly a gross correlation between average differential heats and proton affinities for both the alcohol and nitrile structural series as well. Higher proton affinities correspond to higher binding energies in both series.

As we have discussed above, we believe that the alcohol differential heats represent a dynamic average of 1:1 and 2:1 complexes. As a result, we feel it is not justified to impose a correlation line on the alcohol data. For example, it is quite possible that the preferred structure of the 1:1 complex is best described as a neutral hydrogen-bonded structure, but that the preferred structure of the 2:1 complex is an ion pair. Sauer has suggested this crossover from hydrogen bonding to ion pairing as a function of coverage based on calculations for water adsorption in H-ZSM-5.³⁶ The proton affinity for H₂O is 723 kJ/mol, but the proton affinity of (H₂O)₂ is ~850 kJ/mol, comparable to ammonia. If the data for neutral and ion-pair complexes correlate with proton affinity with different slopes (vide infra), then there should be a proton affinity threshold where the preferred structure in the complex crosses over from hydrogen-bonded to ion-paired for every structural family. This has some interesting implications for optimizing reaction conditions in zeolite-catalyzed chemistry. Since the ion-pair structure should have the steeper slope, and the addition of a second molecule to the adsorbate structure will in general increase the proton affinity, preference for the ion-pair structure and hence ionic intermediates in reaction chemistries should be more favorable at higher coverages.

Unlike the alcohols, 1:1 complexes do form preferentially for nitriles, and it is interesting to compare the differential heats with those of the amines. The first question is how to draw the correlation line for the nitriles. We choose not to include trichloroacetonitrile in the correlation because the comparison of H-ZSM-5 and silicalite data implies that there is no specific interaction with the Brønsted-acid sites for this adsorbate at a stoichiometry of 1:1. Furthermore, we choose not to include butyronitrile in the correlation because the average differential heats of adsorption for this molecule lie significantly above those of the sterically smaller nitriles, propionitrile and isobutyronitrile, which have similar proton affinities. It seems likely that the same secondary interactions are at work for butyronitrile as those that cause *n*-butylamine to deviate from the amine correlation line. The resulting line for the remaining four nitriles is given by $-\Delta H_{\text{ads}} = 0.37\text{PA} - 180$. The slope is therefore significantly less than 1. This is consistent with the expectation that these are polar, neutral complexes not ion-pair complexes like the amines and that the charge-stabilization effects of the substituents will be attenuated relative to the corresponding gas-phase ions.

Meot-Ner has shown that a single correlation line may be adequate to describe the relationship between dissociation enthalpies of NH⁺...O complexes in the gas phase for both protonated amines and protonated nitriles.⁴⁴ We feel there is justification, therefore, for extrapolating the amine correlation to the proton affinity range of the nitrile family, below ammonia, in order to estimate the binding energies of protonated nitrile-zeolite ion-pair complexes. The observed binding energies lie above the ion-pair energies that are estimated this way by 20–30 kJ/mol. In fact, a better estimate would probably be based on trimethylamine (TMA) rather than ammonia, as a standard, since only a single hydrogen bond is possible in the nitriles as in TMA. Extrapolating a line of slope 1 to lower proton

affinities from TMA leads to even larger deviations of the observed nitrile binding energies from the proposed ion-pair thermochemical model.

We conclude, therefore, that, in the proton affinity range covered by these nitrile structures, ~770–820 kJ/mol, nitrogen bases are likely to be more stable adsorbed as neutrals in 1:1 complexes than as ion pairs. If the nitrile correlation line is extrapolated to higher proton affinities, the ion-pair and neutral hydrogen-bond lines intersect at about 885 kJ/mol for a complex that can form only a single H-bond. Different correlation lines and different intersection points should describe different structural families. A family based on two hydrogen bonds (ammonia line) will show a crossover at lower proton affinity since the stabilizing effect of the additional hydrogen bond will be more pronounced in the ion than in the neutral adsorbate. A complete thermochemical series of ethers, for example, might allow similar conclusions to be drawn about the competition between the two adsorbate types of structures for oxygen bases.

Summary

Calorimetric measurements for a series of nitriles and alcohols on H-ZSM-5 have provided important information on the nature of the adsorption complexes. Each of the complexes is formed through hydrogen bonds. For the nitriles, the heats of adsorption correlate with proton affinity, but the slope of the correlation is less than unity, which is to be expected given that proton transfer is not complete. For the alcohols, the heat of adsorption for the second molecule at the site is similar to the first. This is the result of the alcohols being both hydrogen-bond donors and acceptors and may be important for understanding the reaction chemistry.

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