# Characterization of stoichiometric adsorption complexes in H-ZSM-5 using microcalorimetry

D.J. Parrillo and R.J. Gorte

*Department of Chemical Engineering, University of Pennsylvania, Philadelphia, PA 19104-6393, USA*

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We have used microcalorimetry to examine the stoichiometric adsorption complexes formed by ammonia, pyridine, and isopropylamine at the Al sites in H-ZSM-5. The results show that the heats of adsorption for each adsorbate are constant up to a coverage of one molecule/Al, implying that all of the acid sites in H-ZSM-5 are equivalent in strength. The adsorption energies of the complexes formed by ammonia, pyridine, and isopropylamine were found to be 150, 200, and 240 kJ/mol, respectively. Comparison of these values with a simple potential-energy model which assumes that the heat of adsorption scales linearly with gas phase proton affinities suggests that proton transfer dominates the interaction between the adsorbate and the acid site, but that other factors must also be included.

**Keywords:** Calorimetry; pyridine adsorption; ammonia adsorption; isopropylamine adsorption; proton affinities; zeolite acidity

## 1. Introduction

The acidity of H-ZSM-5 is probably understood better than that of any other zeolite. In the absence of steaming, this material contains strong, Brønsted-acid sites in a concentration equal to the framework Al concentration. The reactivities for a number of reactions, including *n*-hexane cracking, toluene disproportion, methanol dehydration, etc., have been shown to increase nearly with Al content [1]. Well-defined adsorption complexes, corresponding to one molecule/framework Al, have been observed for a series of alcohols [2], amines [3], thiols [4], and for acetone [5]. Furthermore, the reactivity of molecules associated with the Brønsted-acid sites can be understood in terms of simple, proton-transfer chemistry. The dehydration of alcohols [2], the oligomerization of olefins and acetylene [6,7], and the decomposition of thiols [4] can all be understood using a potential-energy model which assumes that zeolite is a simple proton donor and that gas-phase proton affinities of adsorbed species can be used to estimate the enthalpy of adsorption complexes. However, simple, gas-phase, proton-affinity models of acidity obviously have limitations. For example, the models predict the formation of stable carbocations, while spectroscopic measurements clearly demonstrate that charge transfer in the adsorption complex is not complete [8].

Actual measurements of adsorption energies are clearly desirable for placing adsorption-energy models on a firmer footing. While microcalorimetry has been used extensively to measure site heterogeneity in zeolites [9–16], the purpose of our study was to examine, specifically, the enthalpy of formation of stoichiometric adsorption complexes for selected molecules. In this letter, we will report data for ammonia, pyridine, and isopropylamine in H-ZSM-5. The results clearly demonstrate that there is one strong acid site/Al and suggest that the acid sites are equivalent. Comparison between the measured adsorption enthalpies and the values calculated from the proton-affinity model suggest that the primary interaction between the adsorbed molecules and the acid sites in the adsorption complex is due to proton transfer but that additional factors, such as Van der Waals interactions with other parts of the molecule, must be accounted for in order to fully describe the energetics.

## 2. Experimental

The calorimeter used in this study was constructed in our laboratory using a design based on that of O'Neil, Lovrien, and Phillips [17]. The heart of the Calvet-type calorimeter, pictured diagrammatically in fig. 1, consists of two pyrex cubes, one for the sample and one for reference, 2.54 cm on a side. Each cube was surrounded on the four sides and on the bottom by square thermal flux meters. The thermal flux meters, which were obtained from International Thermal Instrument Company, Del Mar, CA, are square, polyimide plates with roughly 100 thermocouples embedded inside for detecting a temperature difference across the plate. Each meter was connected in series with the others, with the output from the five meters attached to the reference cell subtracted from the five on the sample cell. The signal from these transducers was sent directly to an operational amplifier on the ADC board of a microcomputer for data acquisition. The sample and reference cells were slid into cubical holes cut out of a large Al block ($\approx 5$ kg); and a silicone-based, heat-sink compound was used to make sure that there was good thermal contact between the Al block and the transducers and between the transducers and the pyrex cells. This entire assembly was then placed in an oven which could be heated to roughly 600 K. The oven also contained a calibrated volume which was used for dosing a known amount of adsorbate into both the sample and reference cells. The entire volume of the system could be evacuated using a liquid-nitrogen-trapped, mechanical pump and the pressure in each part of the system could be monitored with a capacitance manometer.

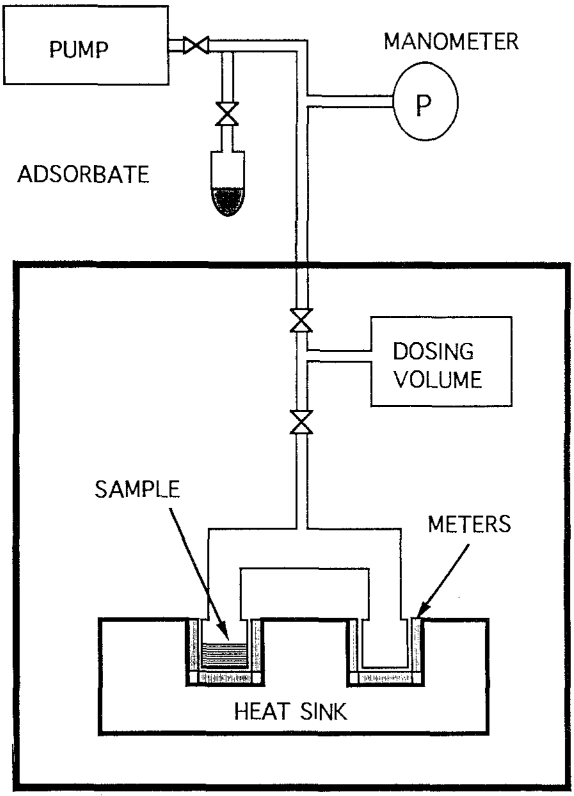

Fig. 1. Schematic diagram of the microcalorimeter used in these experiments.

In a typical experiment, the evacuated system was heated overnight so that a steady baseline signal from the thermal flux meters could be achieved. The dosing volume was then filled to the desired pressure of adsorbent, after which the dose was admitted to the sample cell while monitoring the output from the meters. This signal was integrated with respect to time in order to obtain a relative measure of the heat which had evolved due to the adsorption process. A typical thermogram is shown in fig. 2. The integrated signal was calibrated by passing a current through a Pt wire which had been placed between the pyrex tube and the thermal flux meters. When a known current was passed through the Pt, the baseline rapidly changed to a new value and calibration factors for the transducers could be determined from the baseline shift and the heat generated in the Pt wire. Finally, the pressure in the system was measured after the thermogram was complete in order to calculate how much of the dose had actually adsorbed on the sample. This procedure was repeated until a substantial fraction of each dose no longer adsorbed.

The zeolite sample used in this study was synthesized in our laboratory. X-ray diffraction showed that it was highly crystalline, and scanning electron mi-

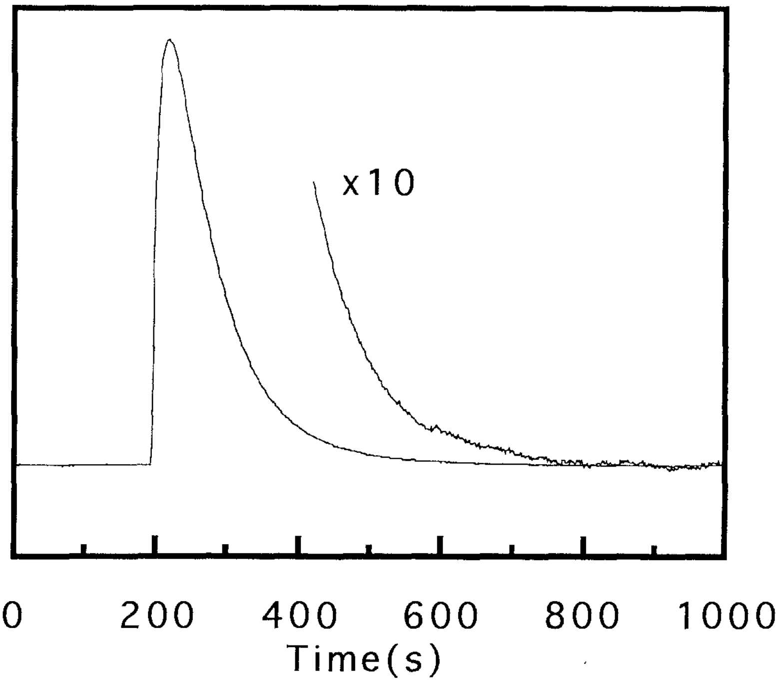

Fig. 2. Signal from the thermal flux meters following a 12 μmol pulse of isopropylamine onto H-ZSM-5 at 480 K.

croscopy showed the crystallites to be roughly spherical and $\approx 10$ μm in diameter. The sample was calcined in dry, flowing air at 820 K for 2 h, after which it was ion exchanged with 1 M $(NH_4)_2SO_4$ at 360 K. The hydrogen form of the zeolite was obtained by again heating the sample in flowing air for 1 h at 770 K. The pore volume of the H-ZSM-5, determined from the gravimetric uptake of *n*-hexane at 298 K and 14 Torr, was 0.185 $cm^3/g$, in reasonable agreement with the ideal value of 0.19 $cm^3/g$. The framework Al content was determined from simultaneous, temperature-programmed-desorption/thermogravimetric-analysis measurements with isopropylamine to be 360 μmol/g (Si/Al = 46), in good agreement with the gel concentration used in the synthesis. (In previous publications, it has been demonstrated that weakly adsorbed isopropylamine desorbs from H-ZSM-5 below 500 K, leaving a well-defined complex at a coverage of one molecule/Al [5]. This complex decomposes to propene and ammonia in a sharp desorption feature between 575 and 650 K and the amount desorbing in this temperature region is an accurate measure of the acid-site density, which is equal to the Al content.) Prior to placing the sample in the sample cell of the calorimeter, it was pressed into thin wafers in order to prevent loss of zeolite during evacuation. Trials on powdered samples demonstrated that this had no effect on the results.

## 3. Results and discussion

All of the calorimetric measurements were carried out at 480 K in order to increase the mobility of the adsorption process. Also, the design of the sample cell allowed for very thin beds, ≈ 1 mm, in order to minimize diffusion limitations in the sample bed [18,19]. Temperature-programmed-desorption (TPD) measurements on small zeolite beds in ultrahigh vacuum (UHV) have shown that ammonia, pyridine, and isopropylamine in excess of one molecule/Al remain on the surface up to approximately 480 K [3], indicating that mobility of physisorbed molecules is small below this temperature. For larger sample beds, the desorption temperature of physisorbed molecules can easily move upward by 150 K. If molecules are not able to move freely throughout the sample, the measured heats for finite adsorption times will include adsorption energies from molecules which are not at the Al sites. In order to test the mobility of molecules in our own sample cell, we measured a TPD curve for ammonia from H-ZSM-5 in the cell and showed that the desorption peak temperature for molecules at the Al sites was ≈ 500 K for a heating rate of ≈ 10 K/min, the same value obtained previously for smaller samples in UHV.

It is also important to consider the mobility of molecules at the Al sites in order to determine how each adsorbate samples the sites in the zeolite. The mobility of these protonated species will be much lower than that of molecules which are not associated with Al sites. For isopropylamine, TPD results indicate that adsorption is irreversible [3]. The molecules are immobile up to 575 K, at which temperature the protonated amine decomposes to propene and ammonia. Pyridine can be removed from the Al sites by heating; however, the rate of desorption from a coverage of one molecule/Al in H-ZSM-5 is insignificant below 600 K, even for small samples in UHV [3]. While surface diffusion may allow faster movement of the molecule between various sites in a given crystallite [20], it is probably not possible for pyridine to move from one crystallite to another in the zeolite bed of the calorimeter. Therefore, adsorption of isopropylamine and pyridine will be essentially chromatographic in the sample, which implies that molecules will not be able to move from weaker sites to stronger sites, even if there is a distribution of acid strengths. In contrast to isopropylamine and pyridine, ammonia adsorption is reversible. As stated above, TPD measurements in our sample cell showed a peak temperature of 500 K for an ammonia coverage close to one molecule/Al, so that movement between sites in the zeolite should be relatively easy for the conditions we used.

The measured heats of adsorption for each of the adsorbates are given as a function of coverage in fig. 3. The results were obtained using a bed size of 0.5 g, with gas doses between 10 and 20 μmol. Results for ammonia are also reported for a 1.0 g sample in order to demonstrate that bed size had no effect on the results. What fig. 3 shows is that the heat of adsorption is essentially constant for each of the adsorbates up to a coverage greater than 300 μmol/g, a value

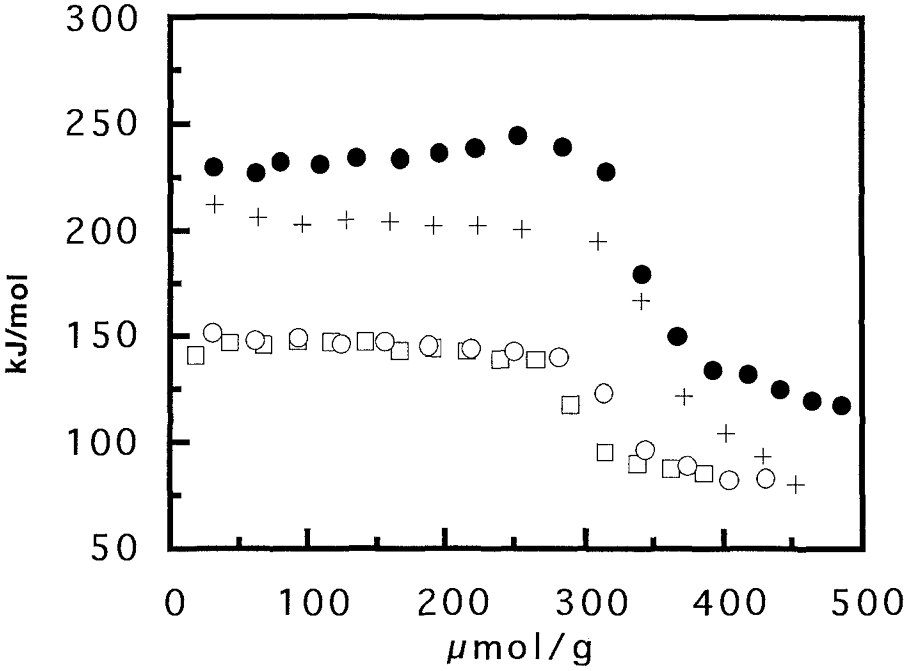

Fig. 3. Heats of adsorption as a function of coverage for ammonia, pyridine (+), and isopropylamine (●) in H-ZSM-5. The results for ammonia were obtained using 1.0 g (□) and 0.5 g (○) of sample.

which is close to one molecule/Al. For higher coverages, the heat drops substantially and we observed a significant pressure rise above the sample with subsequent doses. While the relatively constant heats for isopropylamine and pyridine may be due to chromatographic adsorption in the sample bed (sample calculations indicate that the slight increase in the observed heat of adsorption for isopropylamine is probably due to small losses due to radiation from the top of the zeolite bed), the results for ammonia show that the sites in H-ZSM-5 are energetically homogeneous. Ammonia is mobile at the temperature at which the measurements were made. If there were a distribution in the strengths of the acid sites in H-ZSM-5, the molecules should adsorb at the strongest sites preferentially and there should be a decrease in the adsorption energies as a function of coverage. Using the average heats at coverages below 350 μmol/g, one obtains values for ammonia, pyridine, and isopropylamine of 150, 200, and 240 kJ/mol, respectively.

Comparison of our results with previous work is reasonable where comparison can be made. A range of heats have been measured for ammonia in H-ZSM-5, but most studies have shown an initial heat of adsorption near 150 kJ/mol [9,10,14–16]. A recent study of pyridine adsorption in H-ZSM-5 reported a considerably lower value than we obtained, probably due to a flawed sample; however, it is interesting that this same study gave a value of $\approx 200$ kJ/mol for pyridine on H-mordenite [11].

It is interesting to examine the values for the heats of adsorption of the three compounds in view of the potential energy model which had been derived previously [2]. In that model, it was assumed that the heat of adsorption for a molecule at the acid sites would scale linearly with the gas-phase proton affinity of that molecule. For ammonia, pyridine, and isopropylamine, the proton affinities are 854, 940, and 936 kJ/mol respectively [21]. Using a heat of solution for methanol, Aronson et al. [2] predicted the heat of adsorption of ammonia to be 145 kJ/mol, in almost exact agreement with our observations. Using this same reference, one would predict that the heat of adsorption of pyridine should be 229 kJ/mol and that of isopropylamine should be 225 kJ/mol.

The potential energy model assumes adsorption is completely ionic and only accounts for enthalpy changes due to proton transfer. It also assumes that the interaction energy between the cation, formed by protonation of the adsorbate, and the zeolite framework is independent of the cation structure. Given these major assumptions, the fact that agreement between the measured and predicted values is so good indicates that proton transfer is the dominant factor. Since ammonia is the simplest of the adsorbates, it is reasonable that the proton-transfer picture would work best here; however, recent quantum calculations for ammonia adsorption in H-ZSM-5 have shown that proton transfer is not sufficient to explain the strong adsorption energies for this molecule [22]. Hydrogen bonding with lattice oxygen appears to be very important. For pyridine and isopropylamine, deviations in the measured adsorption enthalpies from those predicted may give additional information about the bonding in the adsorption complex. For pyridine, the predicted value is too high by almost 30 kJ/mol. It is possible that this could be due to pyridine molecules not being able to form additional hydrogen bonds to the same extent as ammonia. Alternatively, it is tempting to suggest that, given the size of the pyridine molecule, there may be steric constraints which lower the adsorption energy slightly in H-ZSM-5. It will be interesting to test this idea with a high-silica, large-pore zeolite. The predicted heat of adsorption for isopropylamine is actually lower than the measured value by 15 kJ/mol. Since the heat of adsorption of propane in high-silica ZSM-5 is $\approx 30$ kJ/mol [23], it is likely that Van der Waals interactions between the alkyl group and walls of zeolite could contribute to the observed heat of adsorption. The slight increase in heat as a function of coverage may be due to attractive interactions between molecules at neighboring sites.

The possibility that adsorption energies may be the result of other interactions in addition to proton transfer suggests that heats of adsorption from a single adsorbate should not be used to compare the acidity of a range of materials. This idea has yet to be tested; however, the use of multiple adsorbates on the same sample, as we have done here, may allow one to subtract out the other interactions so that a true acid–base interaction with the adsorbate can be abstracted from the data. This idea will be examined in future studies.

## 4. Summary

Microcalorimetry measurements for ammonia, pyridine, and isopropylamine on H-ZSM-5 provide further evidence that well defined adsorption complexes form at the Al sites in this zeolite. The concentration of acid sites in H-ZSM-5 is equal to the Al content and the sites appear to be identical in strength. The heats of formation of the adsorption complexes formed by ammonia, pyridine, and isopropylamine in H-ZSM-5 are 150, 200, and 240 kJ/mol respectively. These heats are in reasonable agreement with predictions based on a simple, proton-affinity model for adsorption.

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