Catalysis Letters 12 (1992) 201–212

Microcalorimetric studies of zeolite acidity

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The acidity characteristics of H-ZSM-5, H-Mordenite and H-Y zeolite have been studied by microcalorimetric and gravimetric measurements of pyridine adsorption. H-ZSM-5 and H-Mordenite have Brønsted acid sites of primarily homogenous strength , with H-Mordenite having the stronger sites, whereas H-Y zeolite had Brønsted sites of varying strength. The effects of Na exchange level in H-Y zeolite and high temperature calcination for H-Mordenite have also been examined.

Keywords: Acidity; gravimetry; heat of adsorption; H-Mordenite; H-Y; H-ZSM-5; microcalorimetry; pyridine; zeolite

1. Introduction

The importance of acid catalysts in a wide range of chemical applications is well established [1,2]. Due to the broad application and scale at which these catalysts are used, considerable research has been dedicated towards the characterization of catalyst acidity [3–5]. However, each method of acidity measurement has inherent limitations, and a definitive method for quantitative assessment of catalyst acidity has yet to be developed. Accordingly, studies are needed which advance the understanding of the factors involved in the quantitative measurement of solid acidity.

This note addresses acid catalyst characterization, with particular application to zeolitic catalysts. The experimental approach highlights the use of microcalorimetry, a technique which has been used successfully in the characterization of acid zeolites [6–12]. The microcalorimetric results combined with those of supporting techniques, such as gravimetric measurements and infrared spec-

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troscopy, yield quantitative assessment of acidity. The objectives of this research are three-fold: 1) to quantify the acidity of various zeolites, 2) to study the effect of diverse treatments on the acidity of zeolites, and 3) to describe a multi-technique approach towards the characterization of acid catalysts.

2. Experimental

Heat-flux microcalorimetry was used to measure heats of adsorption of μmole quantities of pyridine on catalyst surfaces at 473 K. The microcalorimeter contained two vacuum cells, one an empty reference cell and another containing the sample. Each dose of pyridine into the cells generated a voltage signal due to heat flux resulting from the heat of adsorption. Integration of this signal provided a determination of the heat released during adsorption, while measurement of initial and final pressures allowed calculation of the adsorbed amount. The dosing was conducted sequentially to a final pyridine pressure of about 5 Torr to titrate the acid sites from highest to lowest strength. The apparatus used in this study was a Setaram C-80 heat-flow microcalorimeter with an attached vacuum system for catalyst treatment and probe molecule delivery; a Baratron capacitance manometer was used for pressure measurement. A complete description of the system can be found in elsewhere [12]. Prior to adsorption of pyridine, the H-ZSM-5 and H-Mordenite samples were pretreated for 4 h in oxygen at 673 K, followed by evacuation for 1.5 h at 673 K. For the H-Y zeolite, oxygen and vacuum pretreatment were conducted at 623 K to minimize zeolite dealumination.

Gravimetric measurements were made to determine the extent of pyridine adsorption at temperatures of 473 and 673 K and pressures ranging from 0.1 to 5.0 Torr. The apparatus used was a quartz spring balance manufactured by Ruska Instruments, connected to a vacuum system for catalyst treatment and admission of pyridine. A Baratron capacitance manometer was used to monitor the pyridine pressure in the system.

The ZSM-5 zeolite was obtained in the proton exchanged form from R. Gorte of the University of Pennsylvania. H-Mordenite, prepared via calcination of the NH_4^+ form for 2 h at 773 K in dry air, was provided by B. Meyers of Amoco Corporation. The NaHY zeolite (which was further exchanged to the proton form) was provided by W.S. Millman of University of Wisconsin-Milwaukee. The Si/Al ratios for the samples were 34, 13, and 2.4, respectively.

Modification of acid character was carried out on two different zeolitic systems. To probe the effect of Na exchange level, NaHY samples with Na levels of 2.24% and 4.31% were prepared by ion exchange with NH_4NO_3 of the above sample containing 8.3% Na. The effect of high temperature calcination in air at 1008 K was studied on H-Mordenite; this sample was prepared by B. Meyers of Amoco Corporation.

3. Results

The differential heat of adsorption of pyridine obtained by microcalorimetry on H-ZSM-5 is shown in fig. 1 as a function of coverage. An important aspect of this curve is that is shows a large number of sites of nearly constant strength, i.e., near 160 kJ/mol for pyridine adsorption. Infrared spectroscopy was used to confirm that these sites are Brønsted acid centers. There is also evidence for some strong sites, evidenced by the initially high differential heats, which may be associated with non-framework aluminium species. At high coverages, weaker adsorption sites near about 100 kJ/mol are filled. This weaker interaction is of the same strength as for pyridine adsorption on silica, which can be characterized as resulting from hydrogen bonding.

The same general features described above are found for the differential heat of pyridine adsorption on H-Mordenite, as shown in fig. 2. At large number of sites at about the same strength is observed on H-Mordenite near 200 kJ/mol, this value being about 40 kJ/mol stronger than those sites of H-ZSM-5. There is also evidence for a small number of sites stronger than 200 kJ/mol, as well as weak sites near 110 kJ/mol. The total number of sites is larger for H-Mordenite compared to H-ZSM-5, as expected from the higher aluminum content on this zeolite.

In contrast to the previous two samples, H-Y zeolite shows Brønsted acid sites of varying strength, as shown by the multiple plateaus in the differential heat curve of fig. 3. These plateaus are representative of acid sites with strengths near 180, 150 and 130 kJ/mol; there is also a small number of sites with

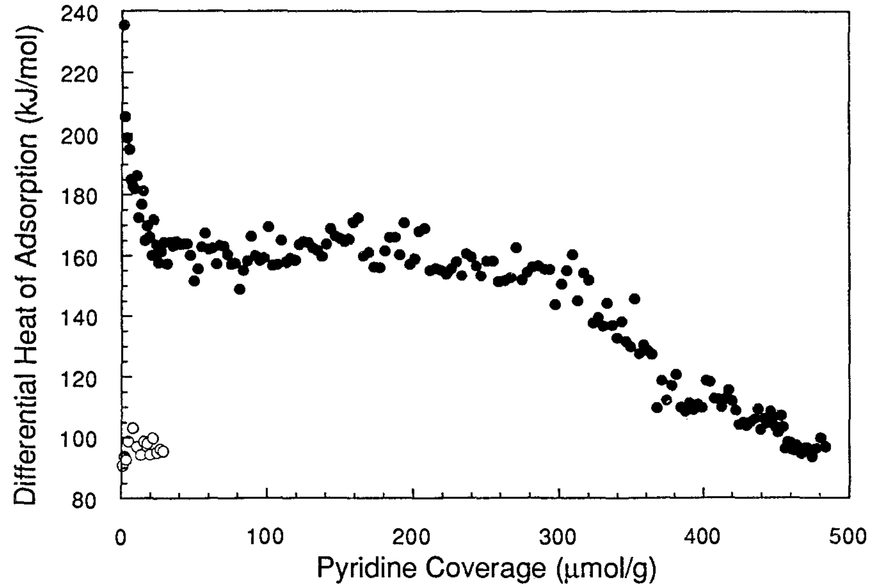

Fig. 1. Differential heat of pyridine adsorption on H-ZSM-5 (●) and SiO_2 (○) at 473 K.

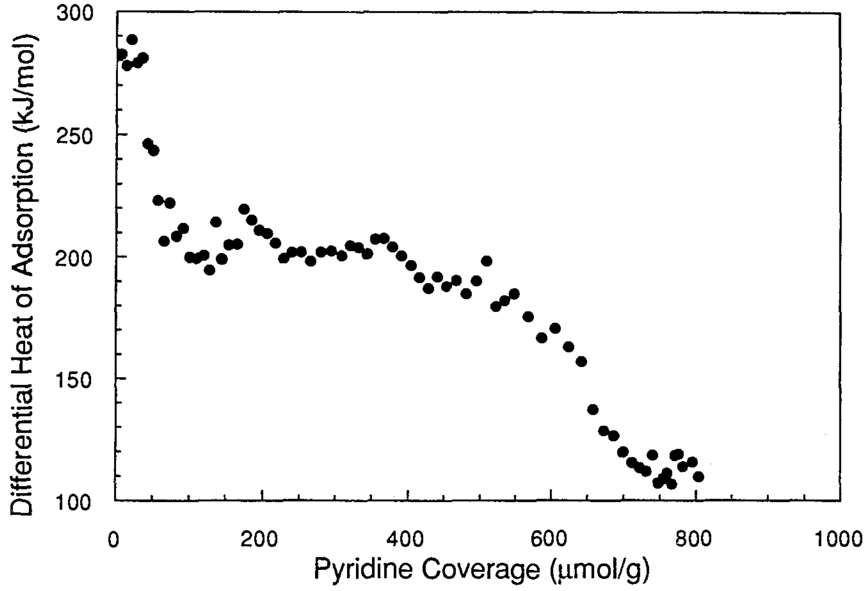

Fig. 2. Differential heat of pyridine adsorption on H-Mordenite at 473 K.

strengths higher than 200 kJ/mol for pyridine adsorption. This fundamental difference between the acid strength distribution of H-Y zeolite compared to H-ZSM-5 and H-Mordenite, namely a wider distribution of Brønsted site strengths, may be related to the higher aluminum content of this sample. It should be noted that the total pyridine coverage for this sample is about half of

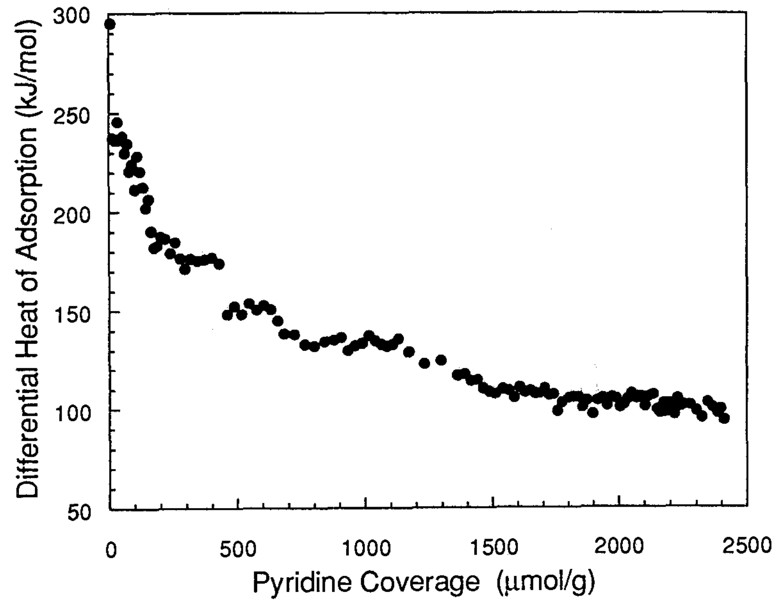

Fig. 3. Differential heat of pyridine adsorption on H-Y zeolite at 473 K.

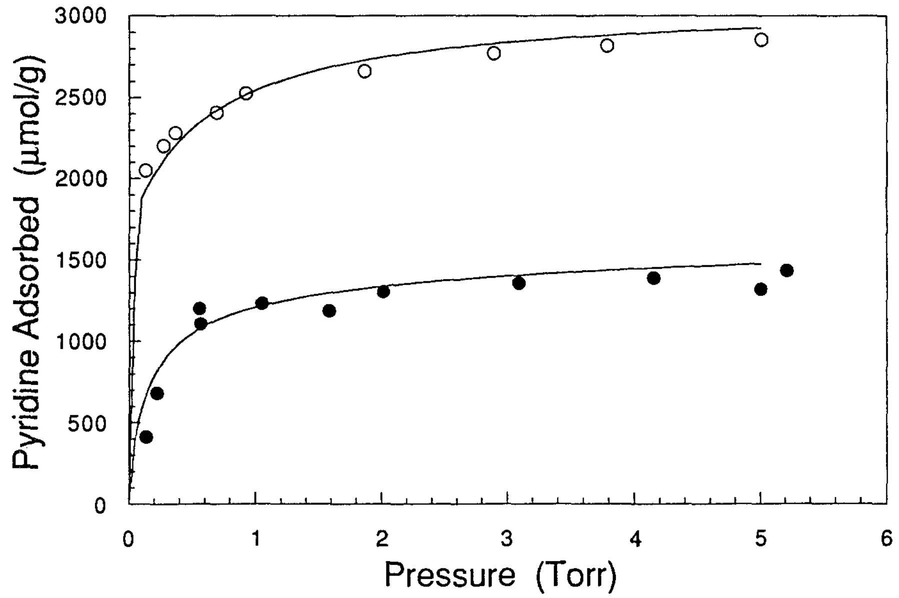

Fig. 4. Pyridine adsorption isotherms on H-Y zeolite at 473 K (o) and 673 K (●) as measured by gravimetry. Fits by combinations of Langmuir adsorption isotherms appear as lines.

that value expected from Si/Al ratio, and this result is probably related to the fact that some of the framework hydroxyl groups are inaccessible to pyridine adsorption because of their location in the lattice [13].

Pyridine adsorption isotherms at 473 and 673 K were obtained gravimetrically for the above three samples. Fig. 4 shows representative adsorption isotherms for H-Y zeolite. An important feature of these gravimetric experiments is that adsorption at high temperatures (673 K) has been employed, whereas microcalorimetric adsorption studies were conducted at the lower temperature of 473 K. Since adsorption-desorption equilibrium between pyridine on the strongest sites and pyridine in the gas phase is not attained at the lower temperature of 473 K, surface diffusion is the mechanism by which the strongest sites may be selectively titrated during sequential exposure of the sample to pyridine [12]. Upon increasing the adsorption temperature to 673 K, adsorption-desorption equilibrium between adsorbed and gas phase pyridine can be more nearly achieved, thus allowing equilibrium isotherms to be approached.

The gravimetric determinations of the saturation coverages of pyridine at 473 K are in good agreement with the microcalorimetric results. At 673 K, pyridine adsorption occurs almost exclusively on sites stronger than about 120 kJ/mol, whereas pyridine adsorption at 473 K is effective for titration of essentially all acid sites. Combinations of Langmuir adsorption isotherm expressions have been used to fit the gravimetric data, as shown in fig. 4. The adsorption equilibrium constants from this fitting procedure were then used with the heat

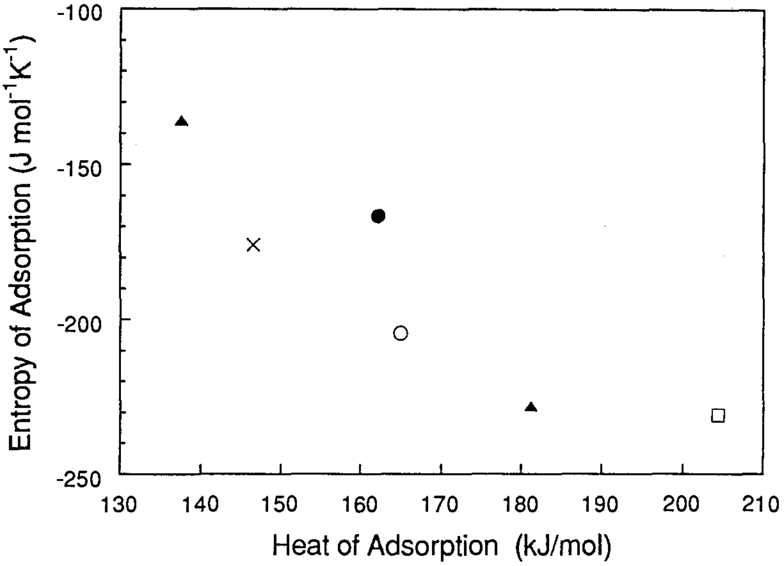

Fig. 5. Heat of adsorption versus entropy of adsorption for pyridine on Brønsted sites of H-ZSM-5 (●), H-Mordenite (□), H-Y zeolite (▲), silica-alumina (×), and an FCC-HY cracking catalyst (o).

of adsorption data from microcalorimetry to estimate entropies of adsorption. This procedure was performed for the above zeolites, as well as for an amorphous silica-alumina sample and a commercial FCC catalyst (Engelhard). A plot of the heat of adsorption for the Brønsted acid sites against the entropies of adsorption for these sites is shown in fig. 5. There is a clear relationship between the strength of the adsorption site and the entropy change for pyridine adsorption on the site. A similar trend has been found previously for hydrocarbon adsorption on X and Y zeolites [14].

The effect of proton exchange level, or sodium content, on H-Y zeolite has been the subject of numerous studies [15–18]. Generally, an increase in acidity with increasing proton exchange has been measured; however, uncertainty exists as to the strength of the acid sites introduced at different exchange levels. Fig. 6 shows the differential heat curves for pyridine adsorption on NaHY zeolite with Na contents of 2.24%, 4.31%, and 8.3% (84%, 68%, and 39% levels of proton exchange, respectively). It can be seen that upon decreasing the sodium content from 4.31% to 2.24%, the last sites to be proton exchanged are rather weak, around 130 kJ/mol. Decreasing the Na level from 8.3% to 4.31% results in fairly uniform generation of acid sites with strengths above 110 kJ/mol.

Fig. 7 demonstrates the effect of calcination at 1008 K on the acidity of H-Mordenite. This treatment causes a significant reduction in the total number and in the strength of the acid sites. The plateau characteristic of a large number of sites of uniform strength has also disappeared. High temperature

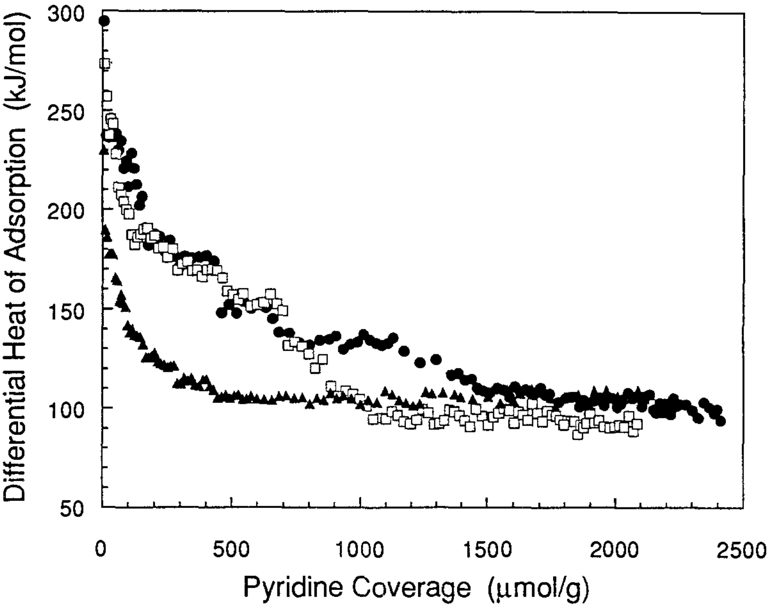

Fig. 6. Differential heat of pyridine adsorption on H-Y zeolite with 2.24 wt% Na (●), 4.31 wt% Na (□), and 8.3 wt% Na (▲).

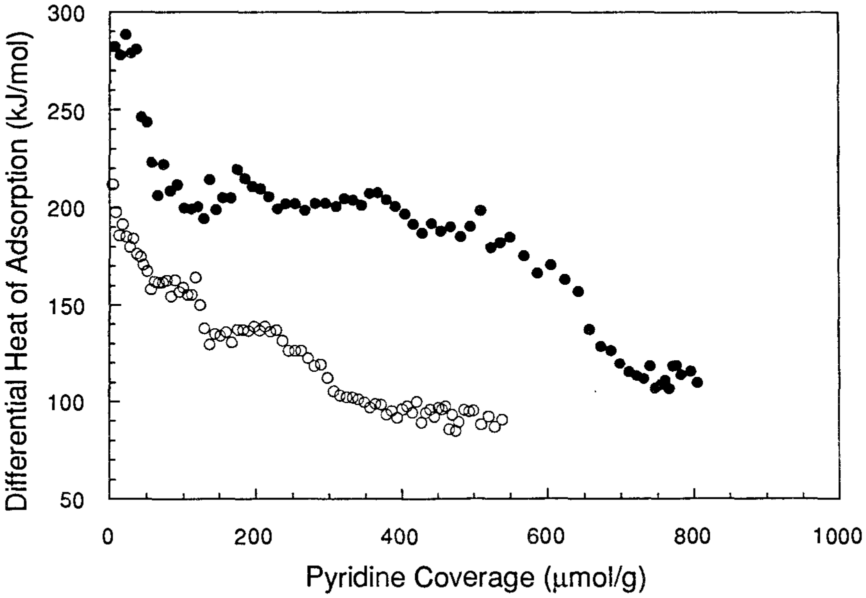

Fig. 7. Differential heat of pyridine adsorption on fresh H-Mordenite (●) and H-Mordenite calcined at 1008 K (o).

calcination is known to induce dealumination and dehydroxylation, both of which are expected to reduce the number of acid sites [19,20].

4. Discussion

The microcalorimetric results on the various zeolites show several important features. The first result is that the H-ZSM-5 and H-Mordenite samples have acid sites which are homogeneous in strength, with H-Mordenite having the stronger sites. In contrast, H-Y zeolite has sites of varying strength, some sites stronger and other sites weaker than the acid sites in ZSM-5. One possible explanation for the heterogeneity in acid strength distribution for H-Y zeolite is that this sample has a higher Si/Al ratio (equal to 2.4). Evidence in the literature suggests that isolated Al framework atoms (having no next-nearest Al neighbors) have the highest strength and that as the number of next-nearest Al atoms increases, the acid strength is likely to decrease [21–24]. Studies of aluminum distribution in Y zeolite suggest that there will be four different acid strengths corresponding to aluminum atoms with 0, 1, 2, or 3 Al nearest neighbors [25–28]. For a Si/Al ratio equal to 2.4, these studies indicate a small number of isolated Al atoms relative to those with 1 or 2 next-nearest Al neighbors. Thus, the sites of varying strength in H-Y zeolite may be a reflection of aluminum topology, i.e. the number of next-nearest neighbor or more distant Al atoms. The H-Mordenite and H-ZSM-5 samples, with their lower aluminum contents, may have fewer interactions of this type, isolated Al atoms comprising the majority of the acid sites.

A quantitative rationalization of acid site strengths is not possible at present; however, it is clear that the heat of adsorption is comprised of at least two aspects [29]. The major factor is the inherent proton-donating ability of the acid site, i.e. the enthalpy of the interaction between the proton and the base. A second factor is the stabilization energy associated with the molecule inside the zeolite lattice and subject to van der Waals interactions. The microcalorimetric measurement of the heat of adsorption of a given molecule contains contributions from both of these factors. Based purely on the aluminum content of the zeolites, it is somewhat suprising that H-Mordenite has stronger acid sites than those of H-ZSM-5. However, adsorption studies of hydrocarbons suggest that the electrostatic fields of different zeolite systems can significantly alter the measured heat of adsorption; these differences can range up to 40 kJ/mol depending on the hydrocarbon adsorbed [30,31].

The entropy of adsorption of a molecule on an acidic catalyst is similarly a measure of two factors. As a molecule adsorbs from the gas phase onto an acid site, there is a partial loss of translational and perhaps also rotational degrees of freedom. The entropy of an adsorbed molecule is also a direct reflection of the mobility of this molecule, as influenced by the environment around the acid site.

The acid site may be configured such that certain motions are inhibited or the distance between sites may be so great as to limit migration of the adsorbate between acid sites.

The relationship between entropy and heat of adsorption is shown in fig. 5. As expected, the stronger the interaction between the acid site and adsorbed molecule, the lower is the mobility of the adsorbed molecule. The fact that the relationship is not strictly linear may be reflect the effect of varying catalyst morphology on the entropy of adsorption. As more zeolites are studied, the influence of zeolitic framework on entropy of adsorption may be clarified.

The studies of modified zeolites reported here demonstrate that there are several means of modifying the strength and number of acid sites and that these changes can be monitored quantitatively. In particular, increasing level of proton exchange results first in a fairly uniform increase in the number of acid sites with strength above 110 kJ/mol. The last sites to be generated have strengths near 130 kJ/mol. Catalytic studies over this series of zeolites may provide clues as to the catalytic properties of stronger versus weaker sites for different reactions. High temperature calcination is a well-known method of reducing total acidity via dehydroxylation and dealumination. Infrared spectroscopic studies of these samples show a much higher population of Lewis acid sites on the calcined sample, while the microcalorimetric results shown for H-Mordenite give a quantitative assessment of the changes in acid site strength.

Several general comments can be made about acid catalyst characterization from these studies of various acidic zeolites. Four acidity features that are likely to play an important catalytic role are listed as follows: the strength of sites, the entropy of adsorption on the sites, the number of sites having a given strength, and the type of acid site, i.e. Lewis or Brønsted. In this study, microcalorimetry has been used to provide information about the strength of adsorption sites and their number. Gravimetric measurements have been used to support these acid strength assessments and to provide adsorption isotherms. The entropy of adsorption has then been estimated from the adsorption equilibrium constants obtained from fits of adsorption isotherms to the gravimetric data and from the heat of adsorption data obtained microcalorimetrically. Finally, infrared spectroscopy of adsorbed pyridine has been used to distinguish Brønsted from Lewis acid sites. The slate of techniques used in this study is not unique, but the idea of using multiple techniques to gather information about the various acidity features is paramount. The approach highlighted here is not limited to simple catalyst systems. Recent work on FCC catalysts modified by steam treatment has demonstrated that these techniques [32] as well as temperature programmed desorption of 2-propanamine [33] can be used to examine quantitatively industrial catalysts with complex acidity features.

5. Conclusions

Microcalorimetry and gravimetric measurements have been used to determine the heats and entropies of pyridine adsorption on H-ZSM-5, H-Mordenite and H-Y zeolites. These experiments allow quantitative comparisons to be made between the strengths of the acid sites on these catalysts. In particular, H-Mordenite and H-ZSM-5 possess predominantly Brønsted sites of uniform strength, with H-Mordenite having the stronger sites. In contrast, H-Y zeolite has Brønsted sites of varying strength, perhaps due to the higher aluminum content of this sample. Acid strength distributions of various modified zeolites have also been measured by microcalorimetry. These studies demonstrate that the acid character of zeolite catalysts can be significantly altered by exchange level and thermal treatment, and that such changes can be monitored quantitatively. Finally, effective characterization of solid acidity requires a combination of various techniques to provide information about the strength of sites, the entropy of adsorption on the sites, the number of sites having a given strength, and the type of acid site.

Acknowledgements

We wish to acknowledge the financial support of the Office of Basic Energy Sciences of the Department of Energy and Graduate Fellowship from the National Science Foundation for one of us (DTC). We also wish to thank R. Madon, R. Gorte, W.S. Millman, W. Haag and B. Meyers for valuable discussions during this work.

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