Thermogravimetric and microcalorimetric studies of ZSM-5 acidity

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The combination of thermogravimetry, microcalorimetry and infrared spectroscopy studies of pyridine adsorption has been used to characterize the acidity of a ZSM-5 catalyst. The majority of the acid sites are Brønsted acid centers associated with framework Al species, with heats of pyridine adsorption equal to 140 kJ/mol. Non-framework Al species in the zeolite sample of this study eliminate an approximately equal number of Brønsted acid sites. These non-framework Al species also produce strong Lewis acid sites with pyridine adsorption heats greater than 140 kJ/mol, as well as weak adsorption sites (e.g., weak Brønsted acid sites or hydrogen bonding sites) with heats equal to 90–140 kJ/mol.

Keywords: Acidity; zeolites; microcalorimetry; thermogravimetry; pyridine adsorption

1. Introduction

Aluminosilicate zeolites are of importance in the conversion of hydrocarbons in the chemical and petrochemical industries, e.g., catalytic cracking, isomerization, methanol to gasoline. The unique catalytic properties of these materials are mainly attributed to their acidic properties. While the quantification of these properties has been the focus of numerous studies, the characterization of catalyst acidity is difficult because of the possible presence of Lewis and Brønsted acid sites and the possible existence of a distribution of acid site strengths.

The present pater utilizes a combination of microcalorimetry and thermogravimetry to characterize the acidity of a ZSM-5 zeolite catalyst. Microcalorimetric measurements of the differential heat of adsorption of a basic molecule as a function of the adsorbate coverage provide quantitative information about the acid strength distribution. Thermogravimetric measurements of the extent of adsorption at different temperatures and pressures give an assessment of the number of acid sites, as well as equilibrium constants for adsorption on the various acid sites.

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Pyridine is the basic probe molecule employed in the present study. We will also use infrared spectroscopy of adsorbed pyridine to distinguish between adsorption on Lewis and Brønsted acid sites.

An issue that we will address is whether the differential heat of pyridine adsorption depends on the adsorbate surface coverage. For example, Deeba and Hall [1] conducted thermogravimetric measurements of pyridine adsorption on a series of amorphous silica/alumina catalysts, and they observed that the isosteric heat of pyridine adsorption decreased with increasing pyridine coverage. In a similar study, Boudart et al. [2] observed a range of isosteric heats of ammonia adsorption on a HNa-Y zeolite catalyst. In the present paper, we will extend these thermogravimetric measurements to a ZSM-5 zeolite sample and compare the results from these measurements with microcalorimetric data.

2. Experimental

The zeolite sample studied was powdered ZSM-5 with a Si/Al ratio 33, obtained from I. Filimonov at Moscow State University. Chemical analysis (Galbraith) of the ZSM-5 zeolite sample showed 452 ± 20 μmol/g Al, 8 ± 1 μmol/g K, and 36 ± 2 μmol/g Na. Magic-angle spinning ^{27}Al NMR spectra were obtained on a Chemagnetics CMC-300A spectrometer at 78.04 MHz using spinning speeds of 2120 and 2663 Hz. Nine-degree pulses of 0.5 μs and recycle delays of 500 ms were used to accumulate at least 6000 scans for each spectrum. According to the NMR spectra, 14.9 ± 2.0% of the aluminum cations were present in an octahedral coordination, the balance being tetrahedrally coordinated.

Microcalorimetric measurements of the differential heat of pyridine adsorption were carried out using a Calvet-Tian heat-flux calorimeter (Setaram C80) operated at 473 K. Detailed descriptions of this apparatus and the experimental procedures have been presented elsewhere [3].

Thermogravimetric measurements were obtained using a quartz spring (Ruska Instruments) microbalance. A 370 mg pellet (dry weight) of the zeolite was pressed at 10 000 psi and placed in a quartz pan suspended from the spring. The spring had a maximum extension of 500 mm and a sensitivity of 1.116 mm/mg. The quartz spring and sample pan were enclosed in a glass column connected to a vacuum system (10^{-5} Torr) and gas handling apparatus. A water jacket around the column allowed for temperature control of the spring at 300 ± 3 K. A furnace surrounding the portion of the glass column containing the sample pan allowed the zeolite to be treated at temperatures up to 800 K. The temperature was controlled to within 1 K utilizing a thermocouple placed inside the cell, next to the pan. The sample pan was positioned to minimize thermomolecular effects arising from temperature gradients around the cell [4,5]. Elimination of these effects was demonstrated when introduction of helium in the cell at pressures up to 5 Torr caused no measurable pan movement for the full range of experimental conditions.

Pyridine (Aldrich Gold Label) was purified by a freeze–pump–thaw procedure and kept in a glass bulb as a liquid at room temperature. Prior to pyridine adsorption, the sample was first calcined at 723 K for 5 h in flowing oxygen, followed by an overnight evacuation at this temperature. Doses of pyridine were introduced into the microbalance system from the pyridine vapor in equilibrium over the liquid. The flow of pyridine into the system was adjusted to a rate sufficient to maintain approximately the desired pressure of pyridine over the sample. Pyridine uptakes were calculated from spring displacement measurements.

Infrared spectroscopic studies were conducted using approximately 100 mg of zeolite powder pressed at a pressure of 10 000 psi into a 2.5 cm diameter wafer. The wafer was placed in a stainless steel IR cell fitted with CaF_2 windows. A Nicolet 7199C Fourier transform infrared spectrometer was employed in these studies. The zeolite wafer was first calcined at 670 K in flowing oxygen, followed by collection of an IR spectrum at room temperature. The sample was then exposed to 50 m Torr of pyridine at 670 K. Based on the thermogravimetric data, this treatment should lead to pyridine adsorption on only the strongest acid sites of the sample. The cell was then evacuated at 473 K to desorb pyridine that may have adsorbed onto the cell walls, followed by cooling to room temperature for collection of an IR spectrum. The sample was subsequently treated in 1 Torr of pyridine at 473 K, at which conditions the thermogravimetric data indicate that all of the acid sites should adsorb pyridine. An IR spectrum was then collected following brief evacuation at 473 K and cooling to room temperature.

3. Results

Thermogravimetric data were collected in the form of two isobars at 20 and 50 mTorr of pyridine, spanning a temperature range from 473 to 733 K, and one isotherm at 523 K between pyridine pressures of 20 mTorr and 5 Torr. The error involved in these measurements was ±10 μmol/g. The total number of sites, based on the maximum pyridine uptake, was 463 μmol/g.

The collection of thermogravimetric data was slow, sometimes taking as long as several days for equilibration of a single point. Adsorption of pyridine onto the column walls and a leak rate of air into the column of about 1 mTorr/h required an occasional brief evacuation of the apparatus followed by introduction of pyridine into the microbalance. The thermogravimetric data collected in this manner are shown in fig. 1.

The results of microcalorimetric measurements of the differential heat of pyridine adsorption versus pyridine uptake are shown in fig. 2. This plot shows the existence of at least three types of acid sites.

Specifically, the sample contains about 60 ± 20 μmol/g of sites that adsorb pyridine with a heat greater than 140 kJ/mol, while about 230 ± 30 μmol/g of sites adsorb pyridine with a heat of 140 kJ/mol. Finally, the remainder of the sites are

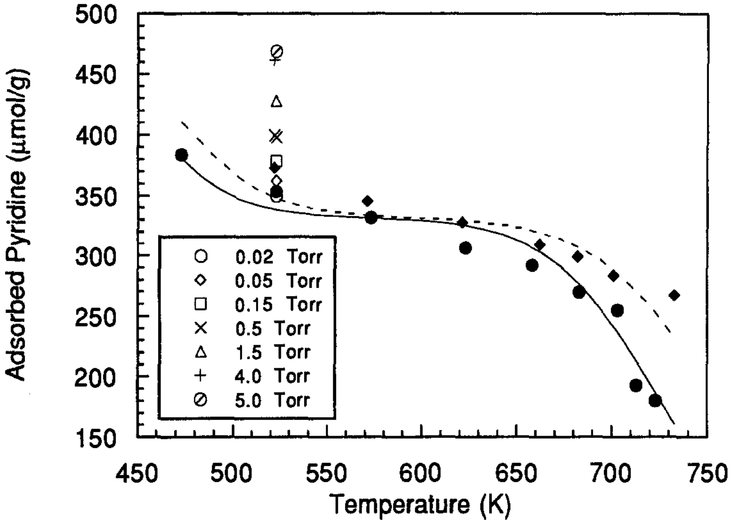

Fig. 1. Pyridine uptakes on H-ZSM-5 measured by thermogravimetry as isobars at 20 mTorr (●) and 50 mTorr (◆), and an isotherm at 523 K (see legend). Fits of the data by combination of Langmuir adsorption isotherms appear as solid (20 mTorr) and dashed (50 mTorr) lines.

weaker and adsorb pyridine with heats from 90 to 140 kJ/mol. The total pyridine uptake corresponding to heats higher than ~ 90 kJ/mol is 440 ± 30 μmol/g.

In view of the microcalorimetric results, the thermogravimetric data were analyzed in terms of three types of acid sites. The strongest sites (> 140 kJ/mol) are expected to be saturated with pyridine at all conditions of this study, and number of these sites (60 μmol/g) is thus subtracted from the thermogravimetric data to give the amount of pyridine adsorbed on the two types of weaker sites. The pyridine uptakes were fitted to a sum of two Langmuir adsorption isotherms, assuming that the heats associated with pyridine adsorption on these sites correspond to those

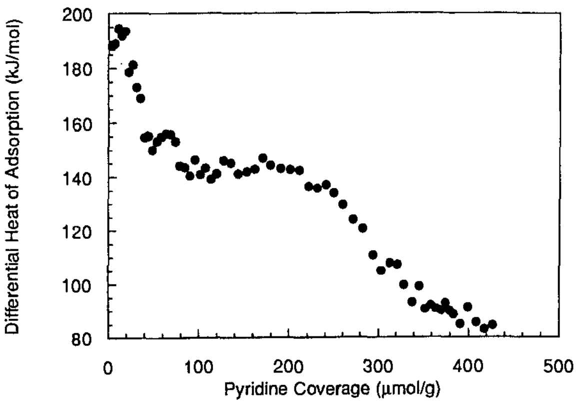

Fig. 2. Differential heat of pyridine adsorption on H-ZSM-5 at 473 K.

values measured calorimetrically (i.e., 90 and 140 kJ/mol). Accordingly, the unknown parameters that were fitted for each site were the number of sites and the standard entropies of pyridine adsorption on these sites. The results of this fitting procedure are shown in table 1 and plots of the predicted isobars are shown in fig. 1.

Fig. 3 shows IR spectra of adsorbed pyridine collected at a resolution of 8 cm^{-1}. These spectra have been ratioed against the spectrum of a clean, calcined sample. Bands at 1446, 1488, and 1600 cm^{-1} can be assigned to pyridine adsorbed onto Lewis acid sites, while peaks at 1488, 1550, and 1635 cm^{-1} correspond to pyridine adsorbed on Brønsted acid sites. In the O–H stretching region of the IR spectrum, two broad bands (more than 50 cm^{-1} at half-width) at 3600 and 3500 cm^{-1} were seen to decrease after the initial exposure of the sample to pyridine. After saturation of the zeolite with pyridine, no bands were apparent in the region between 3200 and 3700 cm^{-1} [6–10].

4. Discussion

The total pyridine uptake of 463 ± 10 μmol/g found thermogravimetrically agrees with the value of 440 ± 30 μmol/g obtained microcalorimetrically, corresponding to the number of adsorption sites that adsorb pyridine more strongly than ~ 90 kJ/mol. These values are also approximately equal to the total number of aluminum cations in the sample, i.e., 452 ± 25 μmol/g.

The solid state NMR characterization of the zeolite sample shows that 15% of the Al is octahedrally coordinated. This value corresponds to about 70 ± 10 μmol/g of non-framework Al cations that may potentially act as strong Lewis acid centers. This idea is supported by the microcalorimetric data which show about 60 ± 20 μmol/g of very strong acid sites. Indeed, extra-lattice Al has been reported in the literature to produce strong Lewis sites [8,11]. The appearance of an IR absorption band near 1450 cm^{-1} after the initial exposure of the sample to pyridine also indicates the presence of strong Lewis acid sites.

A synergistic relationship between framework Brønsted sites and non-framework Al species has been suggested by various researchers [12,13]. Oxo-aluminum cations deposited in channels may produce strong acidity which has been corre-

Table 1
Results of fitting thermogravimetric data

ΔH_1	−140.0 kJ/mol
ΔH_2	−96.5 kJ/mol
ΔS_1	−104±2 J/mol K
ΔS_2	−120±6 J/mol K
n_1	273±12 μmol/g
n_2	132±26 μmol/g

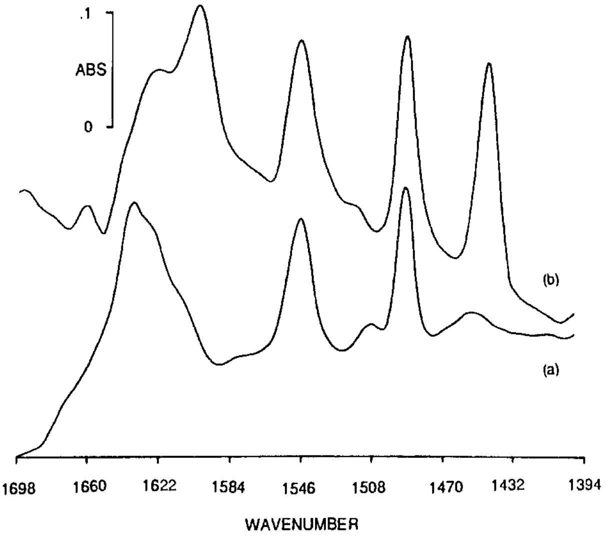

Fig. 3. Infrared spectra of pyridine adsorbed on H-ZSM-5 at coverages of 330 μmol/g (a) and 460 μmol/g (b).

lated with improved catalytic activity for hydrocarbon reactions. The cations, most likely in the form of AlO^+ or $Al(OH)_2^+$, share a bond with the bridging oxygens of Si–O–Al groups, either displacing residing protons or changing the electron density of the OH bond. While we cannot discount the possibility that the strong acid sites observed by microcalorimetry for the ZSM-5 zeolite of the present study are due to strong Brønsted acid sites generated by non-framework Al species, the IR spectra collected at low pyridine coverages suggest that the majority of the strong acid sites are Lewis acid centers.

The 390 ± 20 μmol/g of framework, tetrahedrally coordinated Al cations could give rise to Brønsted acid sites. The sodium and potassium contents of the sample suggest that 44 μmol/g of these framework Al cations may be neutralized by alkali cations. These alkali cations have been found to be weak Lewis acid sites whose occupation by pyridine is signalled by the appearance of an infrared band at 1446 cm^{-1} at high pyridine coverages [7,8]. Accordingly, the maximum number of Brønsted acid sites expected in the sample is 345 ± 20 μmol/g.

The fit of the thermogravimetric data to the sum of two Langmuir adsorption isotherms indicates the presence of 130 ± 25 μmol/g of weak sites and 273 ± 20 μmol/g of strong sites (with an additional 60 μmol/g of very strong sites that remain saturated with pyridine at all experimental conditions). The microcalorimetric results show 240 ± 20 μmol/g of sites with heats of pyridine adsorption corresponding to Brønsted acid sites. The IR spectra also show that the majority of the acid sites for this sample are Brønsted acid centers. In particular, the IR peaks observed at 1635 and 1550 cm^{-1} for intermediate pyridine coverages indicate the presence of pyridinium ions. Also, the suppression of the broad band at 3600 cm^{-1}

upon pyridine adsorption has been linked to adsorption onto hydroxyl groups bridging Al and Si atoms. Thus, we conclude that this ZSM-5 sample contains approximately 230–280 μmol/g of Brønsted acid sites, and this value is smaller than the number of framework, tetrahedrally coordinated Al cations that have not been neutralized by alkali cations (i.e., 345 ± 20 μmol/g).

It is interesting to note that the difference between the number of Brønsted acid sites observed and the maximum number allowed by the framework Al content of the sample is equal to approximately 90 μmol/g, a value that is comparable to the number of non-framework Al cations in the sample. It has been suggested in the literature that non-framework Al cations can cause a strengthening of neighboring O–H bonds [12,13] which would decrease the strength of neighboring Brønsted acid sites, but the argument of a weakened O–H bond has also been posed [14]. We may now suggest that the non-framework Al species in the zeolite sample of this study (60 ± 20 μmol/g) eliminate an approximately equal number of Brønsted acid sites associated with framework Al species. Furthermore, these non-framework Al species produce an approximately equal number of strong Lewis acid sites (coordinately unsaturated Al cations). We finally suggest that these non-framework Al species also produce an approximately equal number of weak acid sites (e.g., weak Brønsted acid sites or hydrogen bonding sites associated with internal silanol groups).

According to the above analysis, the following pyridine adsorption sites are present for the ZSM-5 sample of this study: (i) 60 ± 20 μmol/g strong Lewis acid sites associated with non-framework Al having heats of pyridine adsorption greater than 140 kJ/mol, (ii) 270 ± 30 μmol/g Brønsted acid sites associated with framework Al having a heat of pyridine adsorption equal to 140 kJ/mol, (iii) 44 ± 3 μmol/g weak Lewis acid sites associated with alkali cations having a heat of pyridine adsorption equal to 90–140 kJ/mol, and (iv) 60 ± 20 μmol/g weak acid sites associated with non-framework Al or neighboring species having a heat of pyridine adsorption equal to 90–140 kJ/mol.

A schematic representation of the results of this study is shown in fig. 4. Our observation that the formation of one non-framework Al species causes the loss of two Brønsted acid sites is consistent with other studies of ZSM-5 acidity [9,15]. Here, the result is the generation of one strong acid site and one weak acid site. Accordingly, the total number of acid sites remains equal to the total number of Al species in the sample. In this figure, the two Brønsted acid sites before dealumination of the framework are designated as H_a an H_b, the non-framework Al species formed is AlO^+, the weak acid site created upon dealumination is associated with $Si–OH_a$, and the strong acid site produced is either a Lewis acid center associated with AlO^+ or a Brønsted acid site associated with H_b. As noted above, the results of the present study suggest that the strong acid site is the Lewis acid center, at least for the present sample with respect to its interaction with pyridine.

The standard entropy change of adsorption of pyridine on the Brønsted sites, as extracted from the combination of thermogravimetric and calorimetric data, is

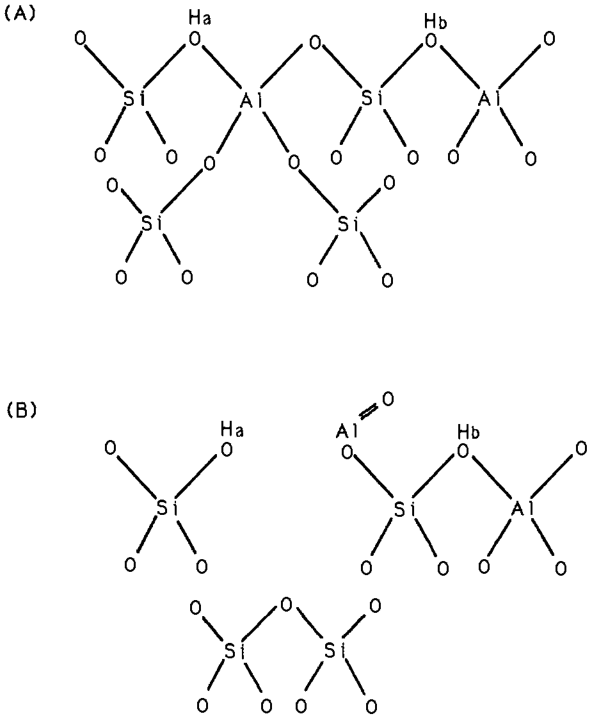

Fig. 4. Schematic diagram of zeolite before (A) and after (B) dealumination, showing the destruction of two framework Brønsted acid sites and the generation of one weaker and one stronger acid site.

−104 ± 2 J/mol K.This value is approximately 60 J/mol K more positive than that previously measured for a different H-ZSM-5 sample [16]. This difference in standard entropy may reflect the lower strength of the Brønsted sites of the sample used in the present study (i.e., 140 kJ/mol in the present study versus 160 kJ/mol for the different ZSM-5 sample).

The calorimetric data of fig. 2 suggest that the differential heat of pyridine adsorption on the Brønsted acid sites is essentially constant (i.e., ~ 140 kJ/mol) with increasing pyridine coverage for this ZSM-5 zeolite sample. One may question whether this result is due to non-specific adsorption of pyridine on acid sites of varying strength, giving rise to an apparently constant heat of adsorption that is an average value. An argument against this possibility is that the differential heat plot shows two distinct regions of strong acidity. Non-specific adsorption of pyridine should not discriminate between these two regions and should instead result in a differential heat plot in which all adsorption sites are incorporated into a single plateau of intermediate heat. The thermogravimetric data presented in fig. 1 also suggest that the calorimetric data are, in fact, representative of the acid-strength distribution for this sample. For example, calorimetric data suggest that the sample contains ~ 340 μmol/g of acid sites that adsorb pyridine stronger than

~ 90 kJ/mol; and, the thermogravimetric results show a plateau near 330 μmol/g for both isobars. The calorimetric data also show that weak sites exist that adsorb pyridine with heats lower than ~ 90 kJ/mol; and, the thermogravimetric results show that the extent of pyridine adsorption becomes higher than 330 μmol/g with increasing pressure at 523 K. Finally, the Clausius–Clapeyron equation can be used with the thermogravimetric results at 20 and 50 mTorr to estimate that the heat of pyridine adsorption is equal to 125 ± 5 kJ/mol at a coverage of ~ 300 μmol/g; and, this value is in agreement with the calorimetric plot in fig. 2 of the differential heat of adsorption versus pyridine coverage.

The observation that the differential heat of pyridine adsorption on this ZSM-5 sample is nearly constant for uptakes between 80 and 220 μmol/g is in contrast to the variable heat of adsorption for pyridine adsorption on amorphous silica/alumina [1] and ammonia adsorption on HNa-Y zeolite [2]. The origin for this behaviour may be that the Brønsted acid sites in this ZSM-5 sample are more isolated compared to amorphous silica/alumina and HNa-Y zeolite that contain higher concentrations of aluminum. In fact, calorimetric measurements of pyridine and ammonia adsorption on such amorphous silica/alumina and HNa-Y zeolite samples show a variable heat of adsorption versus adsorbate coverage [17], in agreement with the published thermogravimetric results [1,2].

Finally, we note that multiple experimental techniques are useful for quantitative characterization of solid acid catalysts, as suggested elsewhere (e.g., refs. [18,19]). For example, microcalorimetry gives an accurate assessment of the heat of adsorption if the temperature is sufficiently high to achieve high surface mobility [3]; however, information about the equilibrium constant of adsorption may be difficult to obtain if the adsorption temperature is not sufficiently high to achieve equilibrium between the adsorbed and gaseous probe molecules. In contrast, thermogravimetric measurements can typically be conducted at higher temperatures and for longer equilibration times compared to microcalorimetry; however, the extraction of information about enthalpy and standard entropy changes of adsorption is not reliable without extensive data, requiring long times for data collection. Also, these measurements must be conducted at temperatures above ~ 700 K and pressures lower than ~ 10 mTorr to probe sites with heats higher than ~ 130 kJ/mol.

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