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Microcalorimetric Investigation of H-ZSM-5 Zeolites Using an Ultrahigh-Vacuum System for Gas Adsorption

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A novel ultrahigh-vacuum system for gas adsorption has been developed for use with a differential microcalorimeter, in order to generate reliable differential heats of adsorption in the low-coverage region of the heat isotherms. It is in this low-coverage region where the strong Lewis sites of zeolites are thought to be detected. In this work, a well-crystallized H-ZSM-5 zeolite which contains very few Lewis sites has been compared with three other H-ZSM-5 zeolites, which contain increasing amounts of intrinsic strong Lewis sites. True Lewis sites were also induced in all of these zeolites by high-temperature dehydroxylation in vacuum. The differential heats of ammonia adsorption were measured, and the results correlated with data from other techniques such as temperature-programmed desorption of ammonia monitored by mass spectrometry and in situ infrared spectroscopy of adsorbed pyridine. The differential heats of adsorption of ammonia on the activated zeolites yielded information about the number and strength of the strong Lewis and Brønsted acid sites. The use of high-vacuum techniques with microcalorimetry allows for accurate determination of the low equilibrium pressures (down to 0.1 Pa) involved with respect to the adsorption of ammonia. Rather small doses of gas can be admitted, thus allowing the more reproducible measurement of an isothermal heat curve. The use of metallic cells also tends to give a rapid heat conductivity. In H-ZSM-5 zeolites, the strong Lewis sites were found to be associated with differential heats of ammonia adsorption at between 185 and 160 kJ/mol and the Brønsted site acid strength was characterized by heats of the order of 157–140 kJ/mol. An NH_4 -ZSM-5 zeolite which was activated at 673 K and possessed very few Lewis sites was observed to have very homogeneous Brønsted acid strength distribution, whereas the other zeolites which contained more intrinsic Lewis sites had differing Brønsted acid strengths of a wider energy distribution.

Introduction

An abundance of techniques is available to probe the nature of the catalytically useful sites of solid acidic materials. Temperature-programmed desorption (TPD) of basic probe molecules,¹ gas-adsorption microcalorimetry using various probe molecules on zeolites,^{2,3} ^1H MAS NMR,⁴ in situ infrared analysis of the O–H vibration and deformation spectral regions of probe molecules,^{5,6} and titration using Hammett indicators⁷ have ranked among the most popular methods. An ever-increasing number of techniques are being developed to enhance the data banks on the acidity of catalysts. One of the more recent developments has been the recognition of the electron spin resonance technique (ESR) which reveals the state of NO molecules adsorbed onto strong Lewis sites.^{8,9} Microcalorimetry still remains one of the most reliable thermodynamic measurement tools, and with new and improved gas adsorption/vacuum technology, this technique is continuing to generate reliable data about the acidic strength and number of the sites in solid catalysts.¹⁰ Most microcalorimetric gas-adsorption systems are not of the ultrahigh-vacuum type (UHV) and very little, to our knowledge, has been reported in the literature about UHV systems in conjunction with microcalorimeters.

In this work, heats of adsorption of ammonia were obtained for four well-characterized NH_4 -ZSM-5 and H-ZSM-5 zeolites using gas-adsorption/microcalorimetric measurements. These were correlated with results from the TPD of ammonia which was adsorbed at the same temperature as for the calorimetric adsorption experiments and with results from in situ infrared adsorption of pyridine. Many papers have been published on the differential heats of adsorption of various probe molecules on H-ZSM-5 zeolites, but most tend not to comment in detail on the initial differential heats. With the gas-adsorption system described in this work, it is hoped to show that these initial heats

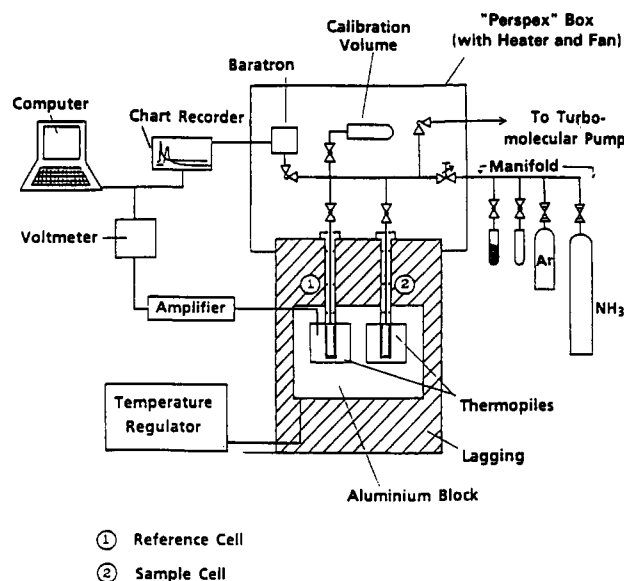


Figure 1. Diagram of the microcalorimetric/gas-adsorption system.

can be reproduced when an ultrahigh-vacuum (UHV) setup is used. Therefore, we can present more reliable low-coverage data and thus, elucidate high-energy Lewis sites that are thought to be responsible for the initial high heats of adsorption.^{10,11} It was also necessary to show that the microcalorimetric gas-adsorption system gives reliable data that is comparable (with respect to higher coverage data) with other microcalorimetric measurements from the literature.

Experimental Section

The microcalorimetric setup is described diagrammatically in Figure 1. The system uses metallic cells which enables good heat conductivity. The gas-adsorption system was constructed from

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TABLE 1: Physical Characteristics of the Zeolites

H-ZSM-5	idealized unit-cell formula	Si/Al ratio (total)	Al _{tot} ^a [atoms/uc]	Al _{oct} ^b [atoms/uc]	Al _{tet} ^b [atoms/uc]
1	(NH ₄) _{2.77} Na _{0.23} Al _{2.8} Si _{93.2} O ₁₉₂	33.4	2.8		2.8
2	H _{2.41} Na _{0.38} Al _{2.8} Si _{93.2} O ₁₉₂	33.7	2.8	0.7	2.1
3	H _{4.04} Na _{0.35} Al _{4.39} Si _{91.6} O ₁₉₂	20.9	4.4	1.9	2.1
4	H _{6.35} Na _{0.07} Al _{6.46} Si _{89.6} O ₁₉₂	13.9	6.5	1.5	5.1

^a Al_{tot} is the total aluminum as determined by wet chemical analysis. ^b Al_{oct} (octahedral Al) and Al_{tet} (tetrahedral Al) from ²⁷Al MAS NMR measurements performed by Dr. Hunger, University of Stuttgart. ²⁷Al MAS NMR results are somewhat uncertain when samples contain large proportions of silanol groups.

stainless steel tubes, interconnected by ConFlat (CF) flanges and stainless steel UHV CF 16 corner valves. All gas-contactable parts were gold-plated including the inner-parts of the valves.

The volumes of the valves were determined by titration and then by ideal gas calibration in both open and closed positions. The system was always calibrated without sample using the gas employed in the experiment and under exactly the same conditions of the experiment. A glass calibration volume attached to a corner valve via a glass-metal connection was also used. The whole system was bakeable and a final experimental vacuum of 2.8×10^{-6} Pa was reproducibly attainable. The whole volumetric system was enclosed in a "perspex" box fitted with a heater and fan system. The chosen equilibrium temperature in the box was usually 312 K. The microcalorimeter and gas-adsorption unit were placed in a thermostated room.

The microcalorimeter [MS 70, Setaram] was calibrated for heat [Joule effect] using a resistor and constant current supply [EJP 30, Setaram]. The heat calibration was always conducted using the experimental cells, both in an empty state and containing sample. These precautions allowed for very stable heat and pressure measurements (and baselines) and very importantly, allowed more accurate determination of the constant, extremely small but nonzero equilibrium pressures. As found with experiments conducted on heteropolyacids, this system remains stable and virtually leak-free over a period of weeks and allows more accurate volumetric determinations.¹² Wall adsorption, although high in a metallic system, appears not to pose problems if a suitable, careful calibration is performed, and this has been shown by comparing the results of two identical experiments but using 0.1 and 0.8 g samples (see also ref 12). It is important that the system remains leak-free, otherwise the equilibrium pressure in the range of 0.1 Pa cannot be accurately determined.

The physical characteristics of the four H-ZSM-5 zeolites may be seen in Table 1 (see also ref 13). The H-ZSM-5(1) sample was actually an NH₄-ZSM-5, and because of the activation temperatures used, the sample was designated as H-ZSM-5 in this work. The samples were lightly pressed and cut into small platelets, which were sieved to a mesh size of between 0.5 and 1.0 mm diameter. Platelets were necessary because powders are difficult to work with in ultrahigh-vacuum (UHV) conditions.

The water-loss and loss of any volatiles of each sample was determined by weight-difference measurements under the same activation conditions as for the microcalorimetry using a Perkin-Elmer TGS-2 thermobalance in high vacuum.

Activations were conducted in the calorimetric cell connected to a turbomolecular-pump (Balzers) separate to that of the microcalorimetric setup. Activations were performed at 673 K, for 2 h, with a heating rate of 5 K/min; the final vacuum of the activation at 673 K was usually 5.0×10^{-6} Pa at 423 K. This pretreatment temperature was suitable to activate the Brønsted and high-energy Lewis sites of the zeolites. Approximately 100 mg of activated sample was used in the microcalorimetric measurements.

A dehydroxylation temperature of 1073 K, for 2 h, with a heating rate of 5 K/min was chosen to increase the concentration of strong Lewis sites. The dehydroxylation was conducted in a quartz glass tube in UHV. The tube was then cooled and the

sample was exposed to the ambient for 1 h before reactivation in the microcalorimetric cells in UHV, at 673 K, as mentioned above.

The microcalorimetric block was set at 423 K for measurement of heats of adsorption of ammonia gas (cylinder, Messer Griesheim, 99.8% pure) which was subjected to three freeze-pump-thaw cycles before being stored over activated molecular sieve.

After activation, the cell was attached (under vacuum) to the gas-adsorption system of the microcalorimeter. The system was pumped down, baked out and allowed to reach thermal equilibrium before admitting successive doses of dry ammonia gas to the sample cell. Each dosing step was monitored for the full integral heat of adsorption evolved by the sample and the pressure drop of the admitted gas. The equilibrium pressure was read at the point where the heat equilibrium was reached and the experiments concentrated on the heats of adsorption associated with strongly acidic sites, i.e., heats between 180 and about 80 kJ/mol. Below 80 kJ/mol the heats of adsorption were representative of physisorption² and will not be discussed in this paper. The microcalorimetric curves (differential heat of adsorption versus amount of NH₃ adsorbed) were well reproducible for the 673 K activation. Curves of samples activated at 1073 K were more difficult to reproduce.

The temperature-programmed desorption (TPD) experimental setup has been described in detail in the literature.¹ To conduct TPD measurements, small zeolite wafers of area 1 cm² were prepared; each wafer was of thickness 10 mg/cm². The wafer was then placed on a thermal conductivity pan which was inserted into an ultrahigh-vacuum system. The system was pumped down for 12 h at room temperature and the sample was activated under the same conditions as for the microcalorimetric experiments, i.e., 673 K, 2 h, rate 5 K/min. The sample was cooled to 423 K before admission of an initial pressure of 1.2 mbar of dry ammonia gas into a volume of 546 cm³ and then expanding into a total volume of 2286 cm³ for 1 h. The sample was then pumped-off for 1 h before beginning the controlled heating programme of 423 K up to 1000 K, with a heating rate of 10 K/min. The ammonia gas was analysed (mass 16, NH₂⁺) by a Balzers QMG 311 quadrupole mass spectrometer with a Balzers QMG 420 multichannel analyzer linked to a personal computer.

Infrared measurements (IR) were made in situ on a Perkin-Elmer PE 225 spectrometer. The zeolites were pressed into self-supporting wafers using a hand press (1 MPa) and were of approximately 8 mg/cm² thickness. The wafers were then placed in a specially designed infrared cell equipped with facilities for activating the sample under high vacuum (10^{-6} Pa) and/or admission of adsorptives.⁶ Spectra were recorded at the temperature attained by the sample in the beam of the spectrometer (approximately 373 K) of (1) the activated zeolites, (2) the zeolites after adsorption of pyridine at 473 K for 2 h, followed by a 1-h pump-down at 473 K in the ranges of 1200–1900 and 3000–4000 cm⁻¹. Ammonia was adsorbed onto the activated zeolites at beam-temperature for 1 h before taking the IR spectrum.

Results and Discussion

Microcalorimetry. The differential heats of ammonia adsorption are plotted against the amount of ammonia adsorbed in

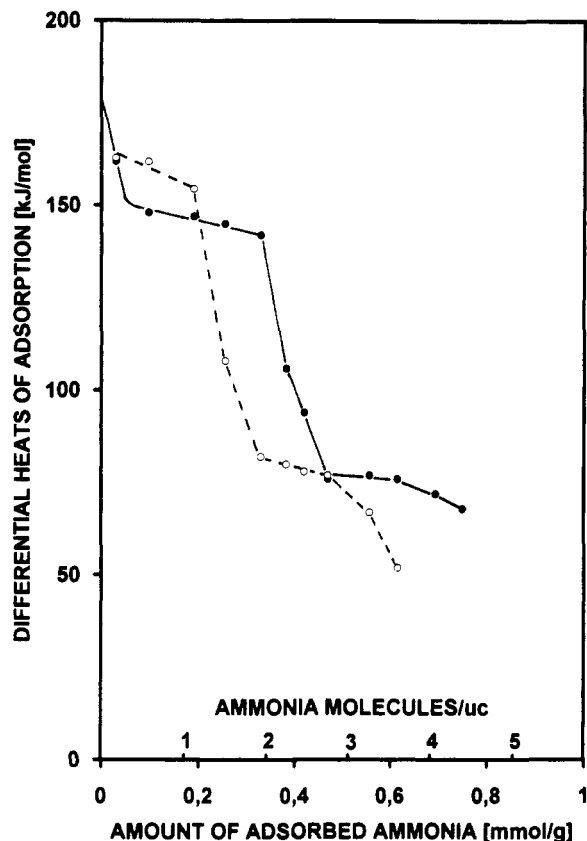


Figure 2. Differential heats of ammonia adsorption on H-ZSM-5(1) at 423 K after activation at 673 K (curve —●—) and 1073 K (curve —○—). The curves represent the average of three sets of data, while the points are taken from only one such set.

Figures 2–5. In Figure 2, curve —●—, the sample of H-ZSM-5 (H-ZSM-5(1)) activated at 673 K shows that, at low coverages (0.25 molecule of ammonia/unit cell (uc)), there are a few sites which evolve high heats upon adsorption of ammonia. The curve then follows a nearly horizontal plateau extending over 2.5 molecules/uc and situated between 150 and 145 kJ/mol, after which the curve drops sharply until a new plateau is reached with heats of about 80 kJ/mol. In the 80 kJ/mol region the heats that are evolved from H-ZSM-5 zeolites tend to be representative of physisorption and indicated the interaction of silanol groups and cations with ammonia.¹¹ The H-ZSM-5(1) sample has been investigated with respect to its aluminum content, and it was found that the aluminum is located almost exclusively in framework positions; see Table 1 for the physical characteristics of the zeolites and also Table 3 for relative pyridine absorbance values of pyridine bound to Lewis and Brønsted sites. The described microcalorimetric curve of isothermal adsorption of ammonia corresponds well to the 0.48 mmol/g (2.8 molecules/uc) total aluminum (as shown in Table 1) assuming that one molecule of ammonia interacts with one acidic site because there are 0.46 mmol/g (2.7 molecules ammonia/uc) of acidic sites giving differential heats of adsorption of greater than 80 kJ/mol. However, it must also be said that the exact number of strongly acidic sites corresponds even more closely with the number of H atoms in the idealised unit cell formula. As can be observed from the extent of the 150 kJ/mol plateau, most of these sites are of a homogeneous acidic strength and are due to the interaction of ammonia with Brønsted acid sites,¹¹ but where the curve drops, there are some sites (approximately 0.13 mmol/g) which have a wide energy distribution, i.e., from 140 to 80 kJ/mol. The general profile of the microcalorimetric curve is in agreement with that produced by Védérine et al.¹¹ for an H-ZSM-5 zeolite of similar Si/Al ratio.

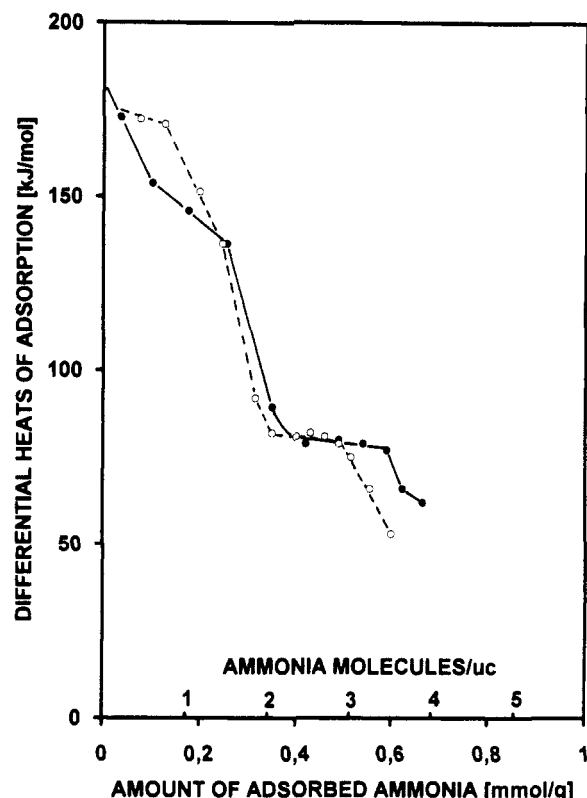


Figure 3. Differential heats of ammonia adsorption on H-ZSM-5(2) at 423 K after activation at 673 K (curve —●—) and 1073 K (curve —○—). The curves represent the average of three sets of data, while the points are taken from only one such set.

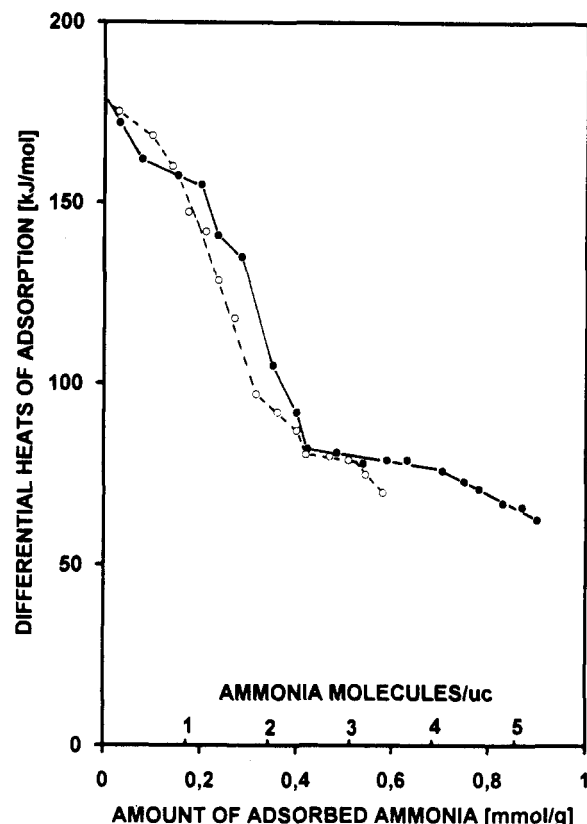


Figure 4. Differential heats of ammonia adsorption on H-ZSM-5(3) at 423 K after activation at 673 K (curve —●—) and 1073 K (curve —○—). The curves represent the average of three sets of data, while the points are taken from only one such set.

Upon dehydroxylation of the zeolite, a new differential heat curve is produced [see Fig. 2, curve —○—]. The plateau is now

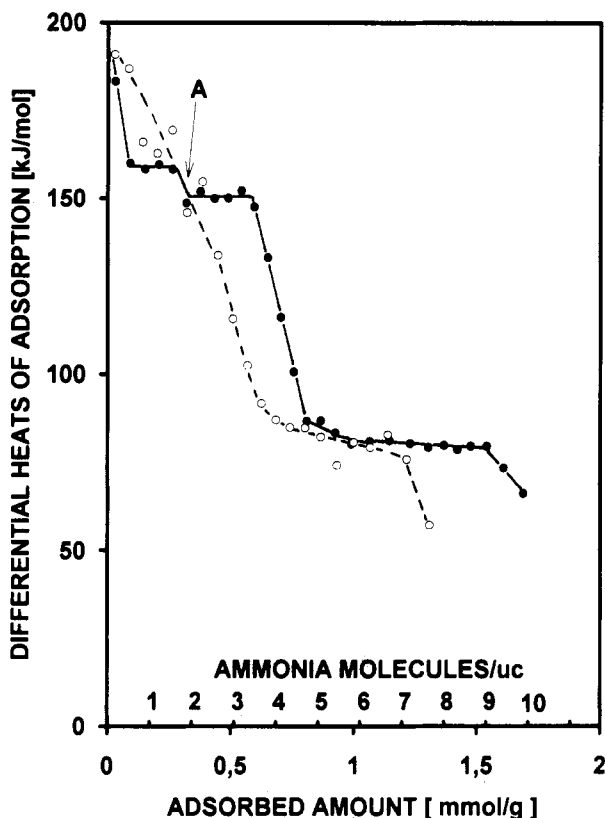


Figure 5. Differential heats of ammonia adsorption on H-ZSM-5(4) at 423 K after activation at 673 K (curve \bullet) and 1073 K (curve \circ). The curves represent the average of three sets of data, while the points are taken from only one such set.

situated at about 163 kJ/mol and continues over 1.6 molecules/uc before dropping in a similar fashion as that for the 673 K activation. In the literature, it has been claimed by several authors that sites with differential heats of ammonia adsorption of greater than 150 kJ/mol in H-ZSM-5 zeolites are strong Lewis sites.^{2,3} In Figure 2, curve \circ , the sites at 150 kJ/mol are no longer observed in the heat isotherm, *vide supra*. Approximately 0.15 mmol/g of acidic sites, amounting to 37% of the original amount present after the 673 K activation, have been lost completely. There has been a large increase in the number of sites evolving differential heats over 150 kJ/mol. These are considered to be heats which have a contribution from both the Lewis sites of high acidic strength (which have been induced by the higher activation temperature) and the remaining Brønsted sites. The sites with 140–80 kJ/mol differential heats have been retained without change.

Figure 3 shows the differential heat curves obtained for the H-ZSM-5(2) zeolite after the 673 K activation (\bullet) and 1073 K activation (\circ). Although the general form of both of the curves is similar to the previously-described H-ZSM-5(1) zeolite, the portion of the curve with heats between 153 and 138 kJ/mol for the 673 K-activated sample, has a more negative slope. The high initial heats (above 153 kJ/mol) are present in larger numbers. These heats are most probably due to high energy Lewis sites which were intrinsically present in the zeolite during the 673 K activation. It can be seen that upon dehydroxylation, the sites with heats between 153 and 138 kJ/mol have been lost and the number of sites which evolve differential heats between 175 and 153 kJ/mol have increased (Figure 3, curve \circ). In the H-ZSM-5(2) zeolite (Figure 3, \bullet), after the 673 K activation, approximately 2.4 molecules/uc of ammonia interact with strongly acidic sites above 80 kJ/mol, 25% of which evolve differential heats higher than 153 kJ/mol. Again, it can be observed that the total amount of aluminum within the sample (2.8 molecules/

uc [see Table 1]) corresponds well with the total number of acidic sites given by microcalorimetry. Upon dehydroxylation, the number of Lewis sites tends to increase as shown by techniques such as pyridine adsorption and IR spectroscopy, and TPD of ammonia, *vide infra*. The differential heats of pyridine adsorption on zeolites have been measured by Chen et al.,¹⁰ whose work has shown that the higher initial heats of adsorption are due to strong Lewis site interaction. The microcalorimetric curve in Figure 3 also shows that the strength of the strong Lewis sites for H-ZSM-5(2) after dehydroxylation has remained the same.

Turning to Figure 4, the H-ZSM-5(3) sample shows a different curve of differential heats of adsorption altogether. The 673 K-activated sample, curve \bullet , shows a considerable intrinsic presence of strongly-acidic Lewis sites, and there are 1.2 sites/uc which interact with ammonia to evolve differential heats between 175 and 157 kJ/mol. This particular zeolite gives rise to a large absorbance of pyridine associated with true Lewis sites (see Table 3). The curve then drops from 157 to 80 kJ/mol (via a small step at 145–140 kJ/mol) showing acidic sites with a large spread of acidic strengths (157–80 kJ/mol) approximating 1.1 molecules/uc in number. A small number of these Brønsted sites are stronger than the strongest Brønsted sites of either of the aforementioned zeolites. This is also clearly shown in the next section, where the TPD curve for H-ZSM-5(3) was found to be much broader than those for the other zeolites and also the maximum of ammonia evolution was found at a higher temperature. The H-ZSM-5(3) activated at 673 K contains a total number of acidic sites amounting to 0.41 mmol/g (or 2.4 sites/uc). It should be mentioned that this does not correspond to the total amount of aluminum as deduced by wet chemical analysis of the sample. From Table 1 it can be seen that the sample contains 4.39 atoms/uc total aluminum but from microcalorimetry, it appears that only 2.0 atoms/uc of that aluminum associated with Brønsted acid sites interacts with ammonia at 423 K. Therefore, approximately 2 sites/uc are not available to interact with ammonia to evolve heats of adsorption above 80 kJ/mol—which is plausible because the sample contains much extraframework Al, part of which replaces acidic protons (see Table 1 and ref 13).

The effect of dehydroxylation of H-ZSM-5(3) is shown in the differential heat curve presented in Figure 4, curve \circ . Compared with the H-ZSM-5(2) and H-ZSM-5(1) zeolites, relatively fewer high-energy Lewis sites have arisen during high-temperature treatment. In fact, some of the strong Lewis sites associated with the original 157 kJ/mol plateau have been sacrificed in order to produce more of the 175 kJ/mol sites. The rest of the dehydroxylated H-ZSM-5(3) zeolite's curve of heat of adsorption (Figure 4, curve \circ) shows that there is no change in the number or energy distribution of the H-ZSM-5(3) sites between 157 and 80 kJ/mol; the small step at \sim 140 kJ/mol remains unaffected. The number of sites with 100–80 kJ/mol has increased slightly. The overall number of acidic sites with energies greater than 80 kJ/mol appears to be the same before and after dehydroxylation. However, the acidic strength distribution of these sites has changed and is complex in nature. The plateau at 80 kJ/mol has been drastically reduced.

The final zeolite of the series under study, H-ZSM-5(4), also shows interesting differential heat curves—note the extended scale of Figure 5 as compared with Figures 2–4, inclusive. Figure 5, curve \bullet , shows a small number of very high energy sites at 185 kJ/mol; however, the 673 K activation reveals two distinct high-energy plateaux. The first plateau is found at 160 kJ/mol and covers 0.22 mmol/g (about 1.3 molecules/uc), and the second plateau is situated at 150 kJ/mol and extends over 0.28 mmol/g coverage (about 1.6 molecules/uc). The 80 kJ/mol plateau represents a large presence of silanol groups. The H-ZSM-5(4) zeolite shows the largest number of strong intrinsic Lewis sites as indicated by the 0.5 molecules/uc ammonia adsorbed on sites to evolve heats of 185–160 kJ/mol. These sites are stronger than any of those seen for the first three samples. Later in the text,

TABLE 2: Most Frequent Activation Energies of Desorption of Ammonia (E) as a Function of Activation Temperature^a

zeolite	T_{act} [K]	$E(1)$ [kJ/mol]	area $x(1)$	$\sigma(E1)$	$E(2)$ [kJ/mol]	area $x(2)$	$\sigma(E2)$	$E(3)$ [kJ/mol]	area $x(3)$	$\sigma(E3)$	$E(4)$ [kJ/mol]	area $x(4)$	$\sigma(E4)$
H-ZSM-5(1)	673	89.0	0.07	2.9	102.0	0.85	5.3	141.0	0.03	10.2	180.0	0.08	7.2
H-ZSM-5(2)	673				96.8	0.87	5.8	116.8	0.07	11.6	186.0	0.16	15.0
H-ZSM-5(3)	673	90.0	0.07	3.0	107.9	0.75	9.0	130.0	0.09	12.0	177.0	0.15	16.4
H-ZSM-5(4)	673				99.1	0.69	6.6	123.9	0.29	12.5	180.0	0.05	11.9
H-ZSM-5(1)	1073	90.0	0.05	3.4	101.8	0.61	5.6	125.0	0.25	13.7	180.0	0.15	11.0
H-ZSM-5(2)	1073				98.8	0.72	6.7	123.6	0.22	11.9	186.0	0.16	13.0
H-ZSM-5(3)	1073	90.3	0.05	3.0	109.9	0.65	10.0	135.0	0.16	10.0	170.0	0.19	16.4
H-ZSM-5(4)	1073				100.8	0.69	7.7	130.0	0.29	11.9	184.0	0.06	11.9

^a The half-widths at half peak height are represented by σ and the areas of each de-convolution peak are also included in the Table for each energy.

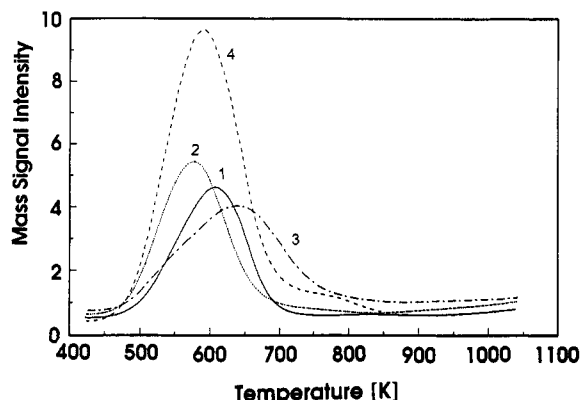


Figure 6. Temperature-programmed desorption of ammonia after activation at 673 K and adsorption/desorption of ammonia at 423 K: curve 1, H-ZSM-5(1); curve 2, H-ZSM-5(2); curve 3, H-ZSM-5(3); curve 4, H-ZSM-5(4).

it will be shown that the plateau at 160 kJ/mol must also be associated with Lewis sites of a homogeneous energy distribution and there is a 1 molecule/uc ammonia adsorption on these sites. The plateau at 150 kJ/mol extends over an adsorbed amount of 1.6 molecules of ammonia/uc showing Brønsted sites of a narrow energy distribution and there are still 2 molecules/uc of acidic sites which evolve differential heats of between 150 and 80 kJ/mol.

Upon dehydroxylation of H-ZSM-5(4), the number of sites of 185 kJ/mol almost trebles and a considerable number of sites with energies greater than 160 kJ/mol appear (Figure 5, curve -O-) at the expense of both of the original high energy plateaux present after the 673 K activation. There is no distinct high-energy plateau for the dehydroxylated zeolite but a large number of sites spanning a wide energy distribution between 185 and 160 kJ/mol, and these sites amount to 2 molecules/uc of adsorbed ammonia. The curve then drops at a slower rate than its counterpart representing the zeolite activated at 673 K. It would appear then that H-ZSM-5(4), activated at 673 K, contains four types of strongly acidic sites; those with energies of between 185 and 160 kJ/mol, which are very small in quantity, sites at 160 kJ/mol and 150 kJ/mol, each amounting to about 1.5 molecules/uc and a lower number of sites of a broader energy distribution in the range 150–80 kJ/mol. From the H-ZSM-5(1) results, we know that the 150 kJ/mol sites are most certainly Brønsted acidic OH groups. However, the H-ZSM-5(3) zeolite has sites above 157 kJ/mol which, after examination of the framework and non-framework aluminum content, were taken to be Lewis sites. Therefore, it could then be proposed that the 160 kJ/mol sites in H-ZSM-5(4) are also high-energy Lewis sites. The total amount of aluminum in the sample of H-ZSM-5(4) amounts to 6.46 atoms/uc (Table 1) and the total amount of ammonia which can be adsorbed giving differential heats of over 80 kJ/mol is similar to this and amounts to 5.8 molecules/uc.

The suggestion that the heats above 150 kJ/mol are actually due to Lewis sites and can be differentiated by microcalorimetric

gas-adsorption measurements, is further substantiated by the fact that the number of sites evolving differential heats greater than 150 kJ/mol increases considerably after the dehydroxylation process in the case of each of the H-ZSM-5 zeolites studied (see Figures 2–5). Taking the energies attributable to Brønsted acid sites for each zeolite after activation at 673 K, as explained above, the respective zeolites may be placed in order of the acidity-strength of their strongest Brønsted sites as follows:

H-ZSM-5(3) (157 kJ/mol) > H-ZSM-5(4)
(150 kJ/mol) > H-ZSM-5(1) (150–140 kJ/mol) >
H-ZSM-5(2) (150–137 kJ/mol)

The H-ZSM-5(3) and H-ZSM-5(2) have the largest site energy distributions, and the other two zeolites have relatively large quantities of homogeneous Brønsted sites.

The order of amounts of high-energy Lewis sites for each zeolite after activation at 673 K is as follows:

H-ZSM-5(4) (1.5 sites/uc) > H-ZSM-5(3)
(1.2 sites/uc) > H-ZSM-5(2) (0.6 sites/uc) >
H-ZSM-5(1) (0.25 sites/uc)

This is in agreement with the TPD results (vide infra, see Table 2, area $x(3)$).

The average strengths of the Lewis sites created after dehydroxylation may be listed thus:

H-ZSM-5(4) (185–160 kJ/mol) > H-ZSM-5(3)
(175–157 kJ/mol) > H-ZSM-5(2) (175–146 kJ/mol) >
H-ZSM-5(1) (163 kJ/mol)

After dehydroxylation, there are no Brønsted sites of homogeneous energy distribution (plateau at 150 kJ/mol) left. Only the acidic sites of broad energy-distribution remain unaffected by high-temperature treatment, i.e., the sites between about 140 and 80 kJ/mol. The reproducibility of the curves of differential heats of ammonia adsorption on dehydroxylated samples is rarely as good as for the samples activated at lower temperatures. This may be explained in several ways in that the dehydroxylation time of two hours may not be sufficiently long to provide homogeneously dehydroxylated samples, portions of the samples may be preferentially dehydroxylated by the heating process or, the reexposure to ambient conditions before reactivation (see Experimental Section) may affect the samples causing them to be inhomogeneous. Whatever the reason for the poorer reproducibility, several microcalorimetric experiments were performed and an average curve from all dehydroxylated samples is presented in this work. No such problems were experienced for the samples activated at 673 K.

Temperature-Programmed Desorption. The TPD curves for the four zeolites activated at 673 K may be seen in Figure 6, curves 1–4, while Figure 7, curves 1–4, shows the normalized TPD curves of the samples that have been dehydroxylated at 1073 K. The relative mass signal intensities of NH_2^+ are plotted as a

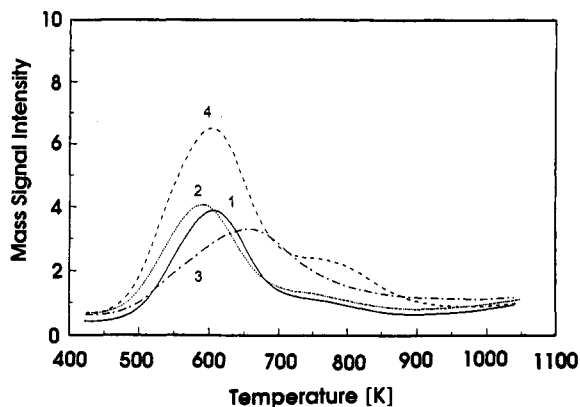


Figure 7. Temperature-programmed desorption of ammonia after activation at 1073 K and adsorption/desorption of ammonia at 423 K: curve 1, H-ZSM-5(1); curve 2, H-ZSM-5(2); curve 3, H-ZSM-5(3); curve 4, H-ZSM-5(4).

function of temperature and are representative of the average amount of ammonia desorbing from sites of different desorption activation energies. The total area under the curve is representative of the total amount of chemisorbed ammonia because the adsorption and desorption of ammonia before the start of the temperature programme was performed at 423 K. All of the curves are normalized to each other and give an indication of the total numbers of acidic sites that desorb ammonia for each zeolite. For example, from the examination of Figure 6, curve 4, it can be seen that the H-ZSM-5(4) zeolite activated at 673 K has, by far, the largest total number of acidic sites. This is also indicated by the curves of differential heats of adsorption "vs" adsorbed amount of ammonia [see Figure 5, curve —●—]. The H-ZSM-5(4) zeolite also shows a second desorption peak at around 780 K indicating acidic sites of a very strong nature. The other three zeolites show shoulders in this region of temperature but they contain fewer of these sites. Kapustin et al.¹⁴ and Auroux et al.¹⁵ have compared microcalorimetric heats of ammonia adsorption with TPD data for ammonia. Further work has been published with respect to IR spectroscopy and TPD of ammonia.^{16,17} The maxima found between 500 and 700 K are thought to be due to ammonia desorbing from Brønsted sites,¹ the width of the curves being related to the energy distribution of the sites in question and again explain the slopes of the plateaux in the differential heat curves. The narrower the TPD peak with a maximum between about 500 and 700 K, the closer the microcalorimetric curve approaches a horizontal plateau. This is precisely what is observed with most of the data presented in Figures 6 and 7 and Figures 2–5. The most prominent example of this is indicated by the H-ZSM-5(3) zeolite, activated at 673 or at 1073 K, producing the broadest TPD curves (Figures 6 and 7, curve 3), and it is also one of the zeolites which produces no well-defined plateau in its heat curve (Figure 4 curve —●—). The rather narrow TPD distributions produced by the other three samples correspond well with their respective differential heat curves indicating almost horizontal plateaux. In this respect, all calorimetric curves agree with the TPD for acid site distribution, except for H-ZSM-5(2), the TPD curves of which, at either activation temperature, are narrow but the heat curves of which, exhibit a slope (Figure 3, curve —●—).

The shoulders found between 700 and 850 K are thought to be due to small numbers of strongly acidic Lewis sites of possibly two types.¹ As previously mentioned, the H-ZSM-5(4) zeolite also has a maximum at 780 K showing the presence of a large number of sites with a high activation energy of desorption. The presence of these sites is also clearly reflected by the differential heat curve of this zeolite between 180 and 160 kJ/mol (Figure 5, curve —●—), at an activation temperature of 673 K. This indicates the presence of high-energy Lewis sites whose energies

seem to be differentiated by microcalorimetry. The second plateau between 2 and 4 molecules/uc ammonia coverage with differential heats of adsorption of 150 kJ/mol (Figure 5, —●—) indicates the Brønsted sites of homogeneous strength distribution and correlates to the TPD T_{\max} of 583 K (Figure 6, curve 4).

Upon dehydroxylation of the zeolites, the nature of both the TPD and differential heat curves change [see Figures 6 and 7, curve 4 and also Figure 5]. After high-temperature treatment, the TPDs of the zeolites now indicate that the number of very strong Lewis sites has increased as indicated by the arising of broad maxima or more clearly defined shoulders in the 700–850 K temperature region at the expense of the Brønsted sites. From the TPD curves in Figure 6, curve 4, and Figure 7, curve 4, the number of the Brønsted sites has been reduced by about 40% as evidenced by the decrease in area of the low-temperature maximum curve; the distribution of the energies of these sites has broadened. The number of sites evolving ammonia to produce the high-temperature maximum has doubled after the dehydroxylation treatment, but the position of this T_{\max} has hardly changed. Therefore, not only are Brønsted sites changed into Lewis sites by the dehydroxylation process but also the energy distribution of the sites that remain spans over a broad range. The loss of the plateaux of heats of adsorption suggests that the OH groups of homogeneous energy (150 kJ/mol) are the sites that turn into Lewis sites. The weaker sites of broader energy distribution (140–80 kJ/mol) are not removed by the dehydroxylation and are still to be seen in both the microcalorimetric curves and in the TPD curves between 500 and 700 K. The calorimetric curve of the dehydroxylated H-ZSM-5(4) (Figure 5, curve —○—) shows an overall decrease in the total number of acidic sites but the number of sites evolving higher heats of adsorption has increased considerably as indicated over the first 1.5 molecules/uc ammonia coverage, and the well-defined plateaux have disappeared. The TPD curve of the dehydroxylated H-ZSM-5(4) (Figure 7, curve 4) shows that the number of sites evolving ammonia and contributing to the high-energy end of the 500–700 K maximum overlap with the number of sites evolving ammonia and contributing to the lower-temperature end of the 700–850 K maximum. The other zeolites in the series showed the same kind of effect in their TPD curves upon dehydroxylation (compare Figures 6 and 7).

The 500–700 K temperature maxima of the TPD curves of all of the H-ZSM-5 samples studied essentially retain their positions after dehydroxylation. This seems to indicate that the strength of the remaining Brønsted sites is not significantly affected by the presence of the newly generated Lewis sites.

To try and group the respective sites according to their activation energies of desorption of ammonia, a deconvolution of each curve was performed after the method of Karge and Dondur.¹ The most frequent energies of activation of ammonia desorption (E) for each zeolite may be seen in Table 2 along with the value σ which represents the half-width of the deconvolution peak and x , which is the area under each deconvoluted curve indicating the number of sites. For example, in comparison with the other zeolites, H-ZSM-5(3) shows the largest line width for the second energy value (E_2) given by $\sigma(E_2)$. A comparison of TPD and microcalorimetry shows that the activation energies of desorption and the differential heats show the same general trend, i.e., the most frequent energies of desorption of ammonia from Brønsted acidic sites before dehydroxylation, calculated by the deconvolution method, are as follows:

$$\begin{aligned} \text{H-ZSM-5(3)} (107.9 \text{ kJ/mol}) &> \text{H-ZSM-5(1)} \\ (102.0 \text{ kJ/mol}) &> \text{H-ZSM-5(4)} (99.1 \text{ kJ/mol}) \geq \\ &\text{H-ZSM-5(2)} (98.6 \text{ kJ/mol}) \end{aligned}$$

In Situ Infrared Spectroscopy and Comparison with Microcalorimetry and TPD of Ammonia. Figure 8 shows, as an example,

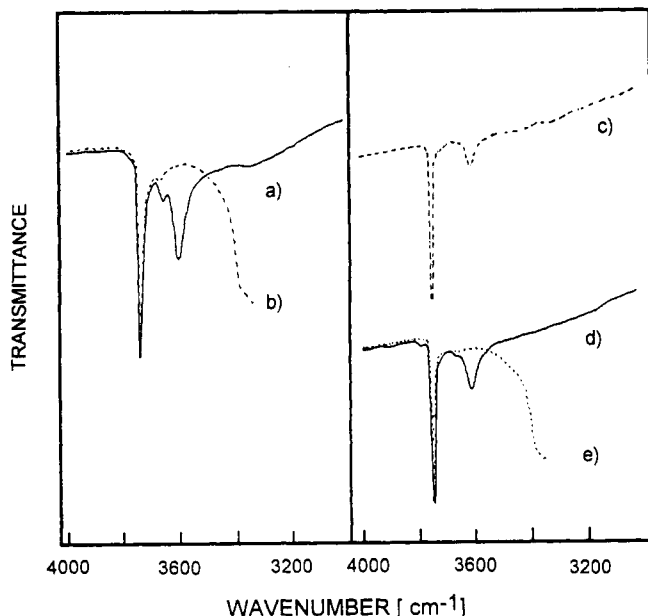


Figure 8. Infrared spectra for H-ZSM-5(3): (a) after activation at 673 K; (b) spectrum of sample shown in (a) after adsorption of ammonia; (c) after activation at 1073 K; (d) the sample shown in spectrum (c) after rehydration in ambient conditions for 1 h and reactivation at 673 K; (e) Spectrum of the sample shown in (d) after ammonia adsorption.

TABLE 3: Normalized Infrared Absorbances

H-ZSM-5	activation temp [K]	normalized absorbances			
		$A_{(3740\text{ cm}^{-1})}$	$A_{(3610\text{ cm}^{-1})}$	$A_{(\text{PyH}^+) \sim 1547\text{ cm}^{-1}}$	$A_{(\text{Py-L}) \sim 1455\text{ cm}^{-1}}$
1	673	0.27	0.35	0.25	0.04
2	673	0.09	0.25	0.24	0.10
3	673	0.57	0.20	0.20	0.16
4	673	0.14	0.36	0.46	0.31
1	1073	0.17	0.22	0.15	0.48
2	1073	0.05	0.16	0.11	0.35
3	1073	0.47	0.10	0.05	0.47
4	1073	0.09	0.06	0.08	0.79

the IR spectra of H-ZSM-5(3) after activation and various treatments such as rehydration, reactivation, and ammonia adsorption. Treatments were chosen so as to simulate those of the microcalorimetric and TPD experiments. After activation, all of the samples exhibited strong OH bands at about 3740 and 3610 cm^{-1} originating from silanol groups (of the external surface and/or crystal defects) and bridging acidic hydroxyls (Brønsted sites), respectively. The absorbances, A , of these bands are, for the sake of comparison, normalized to equal sample thickness (corresponding to 10 mg cm^{-2}) and summarized in Table 3, both for activation at 673 and 1073 K. Additionally, the normalized results of pyridine adsorption on Brønsted sites (see $A(\text{PyH}^+)$ at 1547 cm^{-1}) and Lewis sites (see $A(\text{Py} \rightarrow \text{L})$ at 1455 cm^{-1}) are listed in Table 3.

As well as the aforementioned OH bands, the spectrum of H-ZSM-5(3) exhibited bands at 3660 cm^{-1} which are ascribed to acidic OH groups attached to extraframework Al-containing species.¹⁸

Upon adsorption of ammonia at about 423 K, the IR bands of the silanol groups remained essentially unaffected, as expected, since these groups are known to be weakly or nonacidic. The bands around 3610 cm^{-1} were significantly reduced (H-ZSM-5(1)) or completely eliminated (i.e., H-ZSM-5(2), H-ZSM-5(3) and H-ZSM-5(4)). It was observed, however, that the bands at 3660 cm^{-1} were also almost eliminated after ammonia adsorption, thus they indicate (weakly) acidic sites.

The first half of Table 3 shows that, after activation at 673 K, the H-ZSM-5(1) and H-ZSM-5(4) have the largest number of acidic OH groups followed by H-ZSM-5(2) and H-ZSM-5(3). This sequence of densities of acidic OH groups is approximately reflected by the absorbances of the PyH^+ bands.

Interestingly, the H-ZSM-5(1) sample hardly exhibits any band at 1455 cm^{-1} after the 673 K activation, whereas the other samples show appreciable absorbances at that wavenumber. This means that the H-ZSM-5(1) contains essentially no strong Lewis sites. However, according to the pyridine adsorption data collected in Table 3, the other zeolites investigated contain relatively high amounts of Lewis sites. As suggested by the shoulder at 775 K in the TPD curves presented in Figure 6, some of these Lewis sites are particularly strong in the case of the H-ZSM-5(4) sample, (compare also Figure 7 where, after an activation at 1073 K, a pronounced maximum was observed). These strong Lewis acid sites are obviously involved in producing the plateau at 160 kJ/mol in the case of the H-ZSM-5(4) sample. Similarly, strong Lewis sites contribute to the differential heats of adsorption of higher than about 155 kJ/mol as shown in the initial parts of the heat isotherms of H-ZSM-5(2) (Figure 3) and H-ZSM-5(3) (Figure 4). Thus, the presence of strong Lewis centers is the reason for the striking difference between H-ZSM-5(2) to (4) on the one hand (viz. decrease of differential adsorption heats even at low doses, heterogeneity of acidic site strength) and H-ZSM-5(1) on the other hand (viz. initial plateau of differential heats, homogeneity of strength distribution). The experimental data obtained by microcalorimetric measurements of ammonia adsorption are, at low coverages of the H-ZSM-5 zeolites, markedly affected by the circumstance that the differential heats of adsorption on strong Lewis centers and strong Brønsted sites are relatively close. This will be explained later in the text. However, this fact might render it difficult in some cases to discriminate Lewis and Brønsted sites solely by the adsorption of basic probe molecules and microcalorimetry if no complementary techniques are used.

Upon dehydroxylation, all of the zeolites have lost a considerable proportion of Brønsted sites (indicated by the reduction of the absorbances of the 3610 cm^{-1} peak) as shown in the second half of Table 3. The data in Table 3 shows that there has been a massive reduction in the number of Brønsted acid sites of the H-ZSM-5(4) zeolite because the bands at 3610 and 1546 cm^{-1} have distinctly lower normalised absorbances after evacuation at 1073 K. As a further consequence of the 1073 K activation, the absorbances of the bands associated with pyridine coordinated to Lewis sites have increased as compared with the values given after the 673 K activation for all zeolites. This is, e.g., verified in the curve of differential heat of adsorption of the dehydroxylated H-ZSM-5(4) [Fig. 5, —O—] in that the number of high-energy sites has increased dramatically, but there are virtually no sites at all with energies between 160 and 140 kJ/mol. It can be further seen that the heat curve of the dehydroxylated zeolite crosses the lower activation heat curve point "A" indicated on Figure 5. This point is almost exactly where the Brønsted site plateau at 150 kJ/mol after low-temperature activation began [Fig. 5, —●—]. In view of the complementary IR results, the microcalorimetric heat curves obtained for the H-ZSM-5(2) and H-ZSM-5(3) zeolites provide a reasonable differentiation of the Brønsted and Lewis sites. By contrast, that shown for the dehydroxylated H-ZSM-5(1) sample is not as straightforward to explain in conjunction with the results given by IR experiments both with and without pyridine because over 60% of the Brønsted acidity remains to give a relatively high absorbance for the IR bands at both 1547 and 3610 cm^{-1} (Table 3). In this particular case, we see only a single plateau at 163 kJ/mol in the heat curve of the dehydroxylated sample [Fig. 2, —O—]. This plateau is probably comprised of the average differential heats of adsorption of ammonia on both types of sites, which must be associated with

heats of ammonia adsorption that are not too different (vide supra). This may be substantiated by a simple calculation using the differential heats of adsorption data for Brønsted and strong Lewis sites including the other H-ZSM-5 samples used in this work.

We can assume an idealized differential heat of ammonia adsorption on a Brønsted site of 150 kJ/mol as given by H-ZSM-5(1) activated at 673 K and proven to have relatively few strong Lewis sites at this activation temperature. Then we can assume that the other zeolites, which do contain measurable proportions of strong Lewis sites at the 673 K activation temperature may yield an average heat of adsorption on a strong Lewis site of about 175 kJ/mol. The average of these two heats of adsorption is 162.5 kJ/mol, which is the same as that measured for the H-ZSM-5(1) after activation at 1073 K (Fig. 2, —○—).

Comparison of the absorbances of the 3610 cm^{-1} bands of the H-ZSM-5(2) and H-ZSM-5(1) show that, even though both samples contain the same amount of total Al (Table 1, $\text{Al}_{\text{tot}} = 2.8$ atoms/uc), the H-ZSM-5(1) has about 40% more acidic bridging OH groups (Table 3). If the microcalorimetric curves are reconsidered for these two zeolites after the 673 K activation and adsorption of ammonia at 423 K (Figures 2 and 3, curve —●— in both cases), it can be seen that the H-ZSM-5(2) zeolite has a slightly smaller number of strongly acidic sites. This is shown by the amount of ammonia adsorbed evolving differential heats of over 80 kJ/mol, amounting to 2.7 molecules/uc for H-ZSM-5(1) and 2.3 molecules/uc for H-ZSM-5(2). But as already pointed out, H-ZSM-5(2) contains strong Lewis sites which are evident between 153 and 180 kJ/mol and are ascribed to aluminum extraframework species. H-ZSM-5(2) has, therefore, a somewhat lower content of framework Al compared to H-ZSM-5(1) and, consequently, a lower content of bridging OH groups as indicated by the lower A (3610 cm^{-1}). Infrared results would thus confirm the microcalorimetric curves of differential heat of ammonia adsorption.

Conclusions

In this work it has been shown that the measurement of the differential heats of adsorption of ammonia at 423 K onto various well-characterized H-ZSM-5 zeolites can differentiate high-energy Lewis sites from Brønsted sites and is of considerable value in the enumeration of these sites. The direct measurement of heat is more accurate than production of calculated energy quantities from TPD data which quantifies average activation energies of desorption. Both the number of highly acidic sites and their energies can be determined and differentiated to a large extent using low-equilibrium pressure microcalorimetry with the use of a very good high-vacuum system, especially in the difficult-to-measure low-coverage region, where the Lewis sites in H-ZSM-5 zeolites evolve high heats on adsorption of ammonia. The use of ultrahigh vacuum for these measurements allows for an extremely stable static gas-dosing system and provides greater accuracy in the measurement of pressures as low as 0.1 Pa to provide the data for the initial 0.1–0.2 mmol/g coverages of ammonia, which are essential in the detection of high-energy Lewis sites in differential heat curves. This statement may be extended to the elucidation of small quantities of other sites which are present in zeolites.

In H-ZSM-5 zeolites, the sites which are prone to differential heats of adsorption of ammonia of greater than ~ 150 kJ/mol are due mainly to adsorption on strong Lewis sites. However, it is possible to see that some H-ZSM-5 zeolites have Brønsted sites with energies slightly higher than 150 kJ/mol. The total number of Brønsted acidic sites span a wide energy distribution (~ 150 –80 kJ/mol) in H-ZSM-5 zeolites but it is specifically the groups with energies of ~ 150 kJ/mol which produce the strong Lewis sites upon dehydroxylation. There are sites between 135 and 80 kJ/mol which adsorb ammonia but these sites are not lost

in the dehydroxylation process at all and their nature mostly remains unchanged by high-temperature treatment. Taking the energies attributable to Brønsted acid sites for each zeolite after activation at 673 K, as explained above, the respective zeolites may be placed in order of their Brønsted acidity strength as follows: H-ZSM-5(3) (157 kJ/mol) > H-ZSM-5(4) (150 kJ/mol) > H-ZSM-5(1) (150–140 kJ/mol) > H-ZSM-5(2) (150–137 kJ/mol), where H-ZSM-5(3) has the largest site energy distribution, H-ZSM-5(2) has a smaller site energy distribution and the other zeolites have rather large quantities of homogeneous Brønsted sites. The order of the amounts of strong Lewis sites for each zeolite after activation at 673 K is as follows:

$$\begin{aligned} \text{H-ZSM-5(4) (1.5 sites/uc)} &> \text{H-ZSM-5(3)} \\ & > \text{H-ZSM-5(2) (0.6 sites/uc)} > \\ & > \text{H-ZSM-5(1) } (\sim 0.25 \text{ sites/uc}) \end{aligned}$$

After dehydroxylation, there are very few Brønsted sites of homogeneous energy left that can be differentiated by gas-adsorption microcalorimetry.

It appears that microcalorimetry can yield useful information on the acidity of zeolites, especially when an ultrahigh-vacuum system is used because doses of ammonia can be made with very much less error in the volumetric measurements due to the facility of reading stable, low-equilibrium pressures over long periods of time.

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