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Studies on the Acidity of Mordenite and ZSM-5. 1. Determination of Brønsted Acid Site Concentrations in Mordenite and ZSM-5 by Conductometric Titration

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The Brønsted acidity of H-mordenite and H-ZSM-5 samples of varying proton concentration has been studied using aqueous conductometric titration, IR spectroscopy, and aqueous potentiometric titration. Good agreement is observed between Brønsted acid site concentrations determined by conductometric titration and IR measurements, while indirect potentiometric titration affords acid site concentrations consistently lower than those measured using the conductometric technique. This finding is rationalized on the basis that, in a conductometric titration, all the accessible Brønsted acid sites are directly titrated, whereas in the potentiometric procedure utilized, only those protons which can be ion-exchanged out of the zeolite are titrated. After allowing for the presence of extraframework aluminum in the zeolites (determined by ^{27}Al NMR), the measured acidity for H-mordenite is found to increase linearly with increasing Al content within the range 0–1.5 mmol Al/g but appears to reach a limiting value at higher Al concentrations. For H-ZSM-5, the experimentally determined number of Brønsted acid sites is also found to be linearly dependent on the Al molar fraction within the range measured (0–1.20 mmol Al/g). For both series of zeolite samples, the measured acidity is generally found to be less than the theoretical maximum calculated on the basis of an H^+/Al ratio of 1.

Introduction

Solid acids find a wide range of catalytic applications in oil and chemical conversion processes.¹ The activity of such catalysts is dependent on the number and strength of acid sites on the exposed surface of the solid, and for this reason, the measurement of acidity in solid materials plays an important role in catalyst research and development. To date, a diversity of techniques has been developed for this purpose such as methods based on IR and MAS NMR spectroscopies, the use of Hammett indicators, temperature-programmed desorption of adsorbed bases, microcalorimetry, potentiometric titration in both aqueous and non-aqueous solvents, and rate measurements of acid-catalyzed test reactions. The method and range of application of these techniques has been extensively reviewed.^{2–6} While these techniques can, when used in combination, provide some degree of information on the strength, number, and distribution of the acid sites present, the qualitative nature of many of the techniques means that it is often difficult to obtain accurate quantitative data from them. Alternative analytical methods for the accurate quantification of acidic sites in solid acids are therefore desirable.

Within this context, it is of interest to note that conductometric titration (in both aqueous and nonaqueous media) has been widely used by soil scientists for the determination of hydrogen ion concentrations in clays for at least 4 decades.⁷ However, to the best of our knowledge, this simple technique has not been applied to the measurement of Brønsted acidity in zeolites. Consequently, we have undertaken a series of experiments designed to assess the accuracy and applicability of conductometric titration in the measurement of Brønsted acidity in solid acids of this type. In this paper, we compare the results of acidity measurements made on a series of protonic ZSM-5 and mordenite samples using aqueous conductometric and potentiometric titration and IR spectroscopy. In a sequel,⁸ these results are discussed in the context of possible dehydroxylation and dealumination processes occurring during the preparation of the protonic forms of these zeolites.

Experimental Section

1. Sample Preparation. Mordenite and ZSM-5 samples (ex Conteka) were obtained in either the Na^+ or the NH_4^+ form. Mordenite and ZSM-5 samples in the Na^+ form and varying in aluminum content were brought into the fully NH_4^+ -exchanged form by treatment with excess NH_4NO_3 (1.0 M NH_4NO_3 , 90 °C, 16 h). Mordenite samples of fixed aluminum content but varying NH_4^+ concentration were prepared by addition of the appropriate quantity of 1.0 M NH_4NO_3 (see main text) to a slurry of the sodium zeolite (25 g) in water (300 mL) with stirring and heating (90 °C, 16 h). All samples were washed with deionized water and subsequently calcined in air at 500 °C for 16 h. IR spectroscopy revealed the absence of any residual NH_4^+ ions in the calcined zeolites. Al-exchanged mordenite was prepared by two successive treatments of an ammonium mordenite (1.52 mmol Al/g) with 1.0 M $\text{Al}(\text{NO}_3)_3$ (50 °C, 16 h), followed by washing with deionized water and drying (vacuum oven, 60 °C).

2. Analysis of Samples. Zeolites varying in aluminum content were analyzed for Si and Al by means of X-ray fluorescence. Mordenite samples partially exchanged with NH_4^+ were analyzed for Si, Al, and Na. The calcined zeolite samples were checked for crystallinity by X-ray powder diffraction (Philips PW 1820 powder diffractometer) and for the presence of extraframework aluminum using solid-state ^{27}Al MAS NMR. Spectra were recorded at 130.3 MHz on a Bruker AM 500 spectrometer using a pulse width of 1 μs (ca. 10° pulse angle) and a recycle delay of 1 s. Samples were spun under nitrogen at a rate of 13 kHz. Chemical shifts were referenced to external $\text{Al}(\text{H}_2\text{O})_6^{3+}$ aqueous solution. The amount of extraframework aluminum present was calculated from the total aluminum content and from NMR peak areas on the assumption that it was present as octahedrally coordinated aluminum ($\delta = 0$ ppm), whereas framework aluminum is tetrahedrally coordinated ($\delta = 54.8$ ppm). Additionally, framework aluminum concentrations were determined from ^{29}Si MAS NMR spectra⁹ (after deconvolution of the peaks using the LINESIM program) obtained on a number of the mordenite and ZSM-5 samples. In all cases, the Al concentrations so determined showed reasonable agreement with those deduced from ^{27}Al NMR

spectra (allowing for the fact that framework Al concentrations determined from ^{29}Si NMR spectra essentially represent an upper bound, due to the presence of overlapping SiOH and Si(1Al) peaks⁸).

^{29}Si MAS NMR spectra were recorded on a Bruker MSL 300 spectrometer (59.6 MHz) with single-pulse ($\pi/2 = 4.0 \mu\text{s}$) and proton high-power decoupling. A recycle delay of 20 s was used. Samples were spun at ca. 4 kHz, and all spectra were referenced to Q8M8 (main peak at 11.60 ppm). In cross-polarization experiments (CP/MAS), single contacts were employed using the flipback sequence with spin-temperature inversion. A contact time of 5 ms was used to selectively enhance the Si-OH signals. A recycle time of 4 s was adequate to allow for recovery of proton magnetization. All ^{27}Al and ^{29}Si NMR measurements were recorded on samples which had been rehydrated via storage in a dessicator for 2 days over aqueous NH_4Cl .

3. Titrations. Conductometric titrations were performed using a Metrohm dosimat E 655 and a Metrohm E518 conductivity meter and cell equipped with a PT-100 electrode. A Metrohm 636 titroprocessor and dosimat were used for all potentiometric titrations, together with a Metrohm (B-NS14/15) combined pH and glass electrode.

4. Procedure for Conductometric Titrations. Aliquots of 0.25 mL of freshly prepared 0.1 N NaOH were added to a suspension of the zeolite (1–2 g) in deionized water (100 mL, $T = 290 \pm 2 \text{ K}$) at 2-min intervals (with stirring), the conductance of the mixture being measured immediately before each addition. Hydroxide addition was continued until the readings indicated that the end point had clearly been reached. The conductance readings (in all cases normalized to 293 K) were corrected for the volume increase in the system arising from the addition of the base¹⁰ and the corrected conductance readings then plotted against the quantity of added hydroxide. End points were determined graphically by extrapolation of the straight portions of the titration curves. Particular care was taken in extrapolating that part of the titration curve beyond the equivalence point. At least four experimental points just above the rounded portion of the curve were used for the extrapolation, affording straight lines with a correlation coefficient of routinely ≥ 0.998 .

5. Procedure for Potentiometric Titrations. The zeolite (1–2 g) was stirred with a concentrated solution of NaCl (50 mL, 3.4 M) at room temperature.¹¹ The resulting slurry was filtered and the exchange procedure then repeated. After filtering again, the filter cake was washed with water (100 mL), and the combined filtrates and washings were then titrated potentiometrically against 0.1 N NaOH to a pH of 10.

6. IR Spectroscopic Measurements. Thin self-supporting wafers were prepared using 25–30 mg of zeolite and placed in a stainless steel IR cell evacuated to a pressure of ca. 10^{-6} mbar. The temperature was then raised to 300 °C at a rate of 5 °C/min, kept constant at 300 °C for 16 h, and subsequently decreased to 60 °C, at which temperature an IR spectrum was recorded. In the case of pyridine adsorption experiments, the sample was evacuated at 500 °C for 16 h and pyridine then adsorbed onto it (150 °C, 30 min). After evacuation at the same temperature to remove physisorbed pyridine, the IR spectrum was recorded. Concentrations of Brønsted and Lewis acid sites were determined by integration of the 1545- and 1455- cm^{-1} bands of the adsorbed pyridine, respectively. Peak areas were in all cases normalized to the area of the 1870- cm^{-1} band of the zeolite sample.

Results and Discussion

1. Conductometric Titration of H-Mordenite and H-ZSM-5. Titration curves with well-defined end points are generally obtained when H-mordenite or H-ZSM-5 samples are conductometrically titrated in water against NaOH. Shown in Figure 1 is a characteristic conductometric titration curve obtained for an H-mordenite sample (1.52 mmol Al/g) titrated with 0.1 N

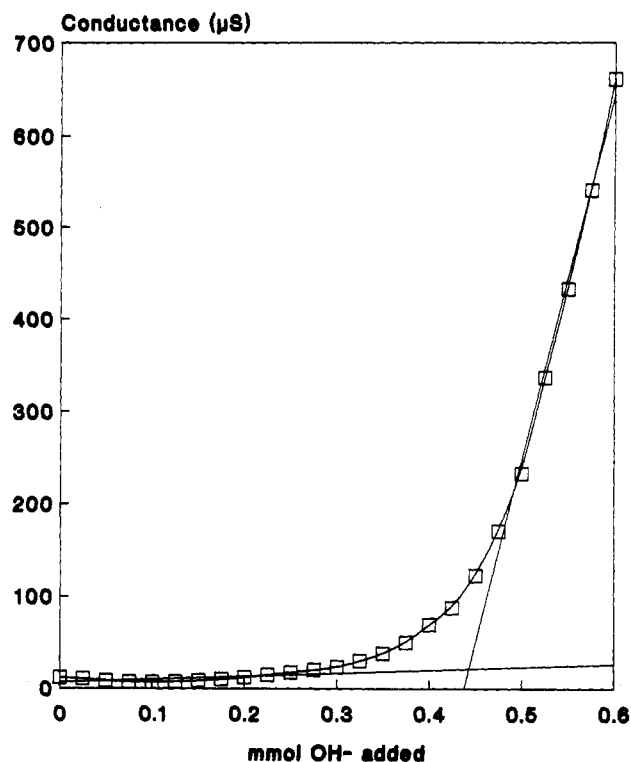


Figure 1. Conductometric titration curve for H-mordenite (1.52 mmol of Al/g) titrated with 0.1 N NaOH.

NaOH at room temperature. In contrast to the high ionic mobilities observed in clay suspensions,^{12–15} the negligible conductance values observed for zeolite suspensions indicate that the H^+ ions inside a zeolite do not possess a significant macroscopic mobility (and hence conductivity) with respect to the suspension. Initial additions of NaOH to the zeolite suspension do not result in any increase in the measured conductance due to the ongoing neutralization reaction, the solution remaining free of ionic species in this phase of the titration. Beyond the equivalence point, the excess Na^+ and OH^- ions added remain in the solution, causing an almost linear increase in the conductance. The curved form of the titration plot in the region of the equivalence point is attributed to the occurrence of hydrolysis reactions¹⁰ and suggests that relatively weak acid sites are present in the zeolite.

For the purposes of this study, conductometric titrations were performed on mordenite and ZSM-5 zeolites of varying Brønsted acid site concentration. In the case of the mordenite samples, two procedures were followed in order to vary the concentrations of acid sites in the samples. In the first procedure, the Na^+ zeolites, varying in aluminum content, were exchanged with excess NH_4^+ ions and subsequently calcined. This methodology was also employed for the ZSM-5 samples. In the second procedure, samples of a Na^+ -containing aluminum-rich mordenite ($\text{Si}/\text{Al} = 6$; 2.3 mmol Al/g) were exchanged with varying amounts (0.2, 0.6, 1.2, 1.8, 2.3 mL/g zeolite) of a 1 M aqueous NH_4NO_3 solution prior to calcination. In this manner, varying fractions of the Na^+ ions were replaced by NH_4^+ ions.

Shown in Figure 2 are the experimentally determined numbers of Brønsted acid sites (expressed in mequiv of H^+ /g) for the H-mordenite samples, plotted against the Al or NH_4^+ content (in mmol/g) as appropriate. Relevant data are given in Table I. The solid line represents the theoretical maximum number of Brønsted acid sites of the various samples, based on a 1:1 ratio of H^+ and aluminum/ NH_4^+ content. In general, the number of Brønsted acid sites determined by conductometric titration is lower than the theoretical maximum, the measured acidity reaching a maximum at an Al/ NH_4^+ content of 1.5 mmol/g and thereafter appearing to remain constant. At this point, it must be stressed that, during a conductometric titration, extraframework alumi-

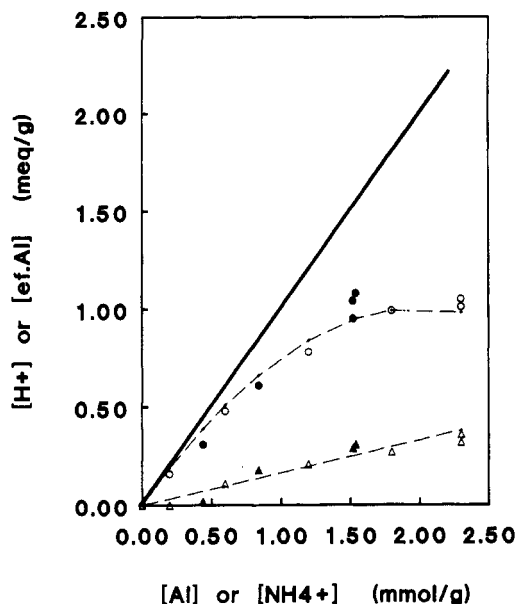


Figure 2. Brønsted acidity (●, ○) as determined by conductometric titration and extraframework aluminum content (▲, △) as a function of the total aluminum content (filled symbols) or the NH_4^+ content (open symbols) of the various H-mordenite samples.

num is titrated in addition to acidic hydroxyl groups (*vide infra*). Owing to the fact that ^{27}Al MAS NMR revealed the presence of extraframework aluminum in all the H-mordenite samples, Brønsted acidity measured for these samples must be regarded as the sum of the concentrations of acidic hydroxyl groups (in mmol/g) and cationic extraframework aluminum species (in mequiv/g).

The results of conductometric titrations of H-ZSM-5 samples varying in aluminum content (and fully exchanged with NH_4^+ prior to calcination) are shown in Figure 3. With the exception of one sample, ^{27}Al MAS NMR showed the H-ZSM-5 samples to be free of extraframework aluminum species (Table I). From the figure, it is apparent that the experimentally determined number of Brønsted acid sites (dashed line) increases linearly with increasing aluminum content within the range measured (0–1.20 mmol Al/g) but is lower compared to the maximum number of sites (solid line). From the slope of the experimental line, an H^+/Al ratio of 0.68 is calculated. This finding is in reasonable agreement with the restricted ion-exchange capacity (ca. 80% of the theoretical value) for K^+ previously observed for a series of H-ZSM-5 samples of varying composition.¹⁶ Additionally, acidity measurements on H-ZSM-5 zeolites using several nonaqueous analytical and spectroscopic techniques have recently been reported by Sato and co-workers.¹⁷ For the ZSM-5 samples employed in their study, the measured acidity was also found to represent ca. 60% of the theoretical maximum calculated on the basis of the aluminum content.

2. Extraframework Aluminum. The existence of extraframework aluminum species in zeolites has been discussed frequently in the literature.^{6,18} Their nature and distribution depend on the initial composition (especially the Si/Al molar ratio) and structure of the zeolite, as well as the severity of the dealumination process. Currently, no comprehensive view can be given concerning the chemical nature of these species. Kühl proposed that the extraframework aluminum species in zeolite Y are present in a cationic form, i.e., AlO^+ , whether or not hexacoordinated.¹⁹ These species would give rise to Brønsted acidity directly according to eq 1 or indirectly by enhancing the Brønsted acidity of other acid



sites, thereby generating "superacid sites".²⁰ Lewis acidic properties have also been attributed to extraframework aluminum

species in mildly dealuminated H-ZSM-5, the presence of these species being of particular importance in cracking reactions.²¹ Extraction of extraframework aluminum by treatment of zeolite samples with aqueous HCl ranging in concentration from 0.1 (zeolite Y) to 5 N (mordenite) has been reported.^{22–24} In these cases, it seems probable that AlO^+ is directly exchanged for H^+ .

In Figure 2, the concentration of extraframework aluminum [ef.Al] (in mmol/g) present in the calcined mordenite samples is shown as a function of the aluminum or NH_4^+ content. It is evident that the amount of extraframework aluminum is proportional to the total aluminum or NH_4^+ content, an [ef.Al]/[Al] (= [ef.Al]/[NH_4^+]) ratio of 0.16 being calculated (correlation coefficient: 0.914). The fact that the amount of extraframework aluminum is also linear to the concentration of NH_4^+ ions in the partially exchanged mordenite samples means that the degree of dealumination is proportional to the number of Brønsted acid sites initially present, rather than to the aluminum content itself. A similar conclusion has been drawn by Suzuki et al.²⁵ They noted that dealumination is quantitatively inhibited by the introduction of alkali-metal cations into an acidic zeolite. This could be understood from the decrease in concentration of acid sites irrespective of the type and location of these alkali-metal ions.

During conductometric titration of an acidic zeolite, octahedrally coordinated extraframework aluminum species disappear. In Table II, the results of an elemental analysis and a ^{27}Al NMR analysis for (octahedral) extraframework aluminum of a mordenite sample before, after, and at the equivalence point of the titration are presented. Of particular note is the observation that, by the time the equivalence point is reached, the octahedrally coordinated extraframework aluminum originally present is no longer detected by NMR, although no aluminum is lost from the zeolite according to elemental analysis. Significantly, ^{27}Al NMR spectra of titrated zeolites contain a new peak centered at 30 ppm (Figure 4), a chemical shift which has previously been attributed by Brunner and co-workers to the presence of nonframework $\text{AlO}(\text{OH})$ (in hydrothermally treated ZSM-5) in which aluminum is in tetrahedral coordination through its proximity to two framework oxygens.^{26,27} We therefore rationalize that AlO^+ ions (representative for cationic extra-framework aluminum) react with added OH^- to give $\text{AlO}(\text{OH})$ in which aluminum is similarly coordinated.

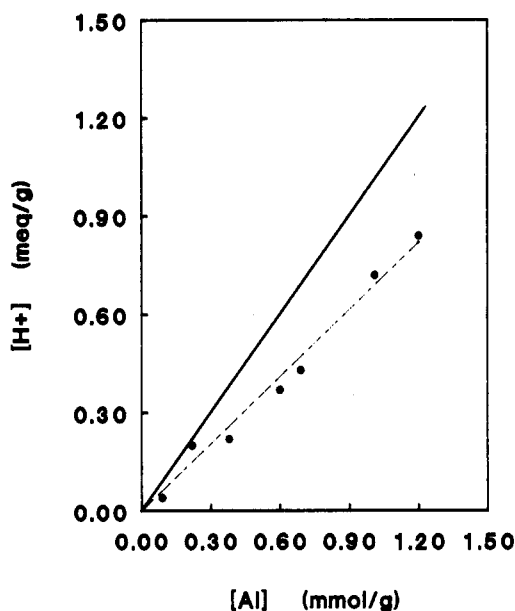
Realumination (i.e., insertion of extraframework aluminum species back into the zeolite framework), resulting from treatment of dealuminated zeolites with 0.1 N aqueous NaOH, has been reported.^{28,29} This could also explain why no octahedral aluminum species were observed after titration. However, in the present work, realumination appears unlikely on the basis that (i) in no cases did the measured pH of the zeolite suspensions exceed a value of 10 during the titrations; (ii) no change in the crystallinity of the zeolites (in all cases 95–100%) was observed after titration (reinsertion of extraframework aluminum has been reported to increase the crystallinity of ZSM-5²⁹); (iii) IR spectra of H-mordenite samples after titration (as well as before titration) contain a strong, broad absorption at 3660 cm^{-1} , attributed to the presence of extraframework Al–OH groups³⁰ (see Figure 7b); (iv) the same spectra show the continued presence of the 3740-cm^{-1} Si–OH absorption band, little changed in intensity; (v) CP/MAS ^{29}Si NMR spectra of the zeolite samples before and after titration show no change in the intensity of the peak occurring at -106 ppm , this corresponding to the presence of both Si–OH groups and Si atoms with one Al atom in the second coordination sphere.³¹ Likewise, framework aluminum concentrations deduced from ^{29}Si MAS NMR spectra (measured with proton high-power decoupling) are unchanged after titration.

From the foregoing, it is evident that a conductometric titration yields the sum of the concentration of Brønsted acid sites (H^+) and extraframework aluminum species (AlO^+). Since cationic

TABLE I: Chemical Analysis for Al, Number of Brønsted Acid Sites as Determined by Conductometric and Indirect Potentiometric Titration, and Corrected Areas of the 3610-cm⁻¹ Absorption Band of H-Mordenite and H-ZSM-5 Samples

| zeolite | [Al], mmol/g | [NH ₄ ⁺], mmol/g | [ef.Al], mmol/g | [H ⁺]/cond, ^a mmol/g | [H ⁺]/pot., ^b mmol/g | IR ^c |
|-------------|--------------|---|-----------------|---|---|-----------------|
| H-mordenite | 0.44 | | 0.02 | 0.31 | 0.21 | 0.45 |
| | 0.84 | | 0.18 | 0.61 | 0.30 | 0.82 |
| | 1.52 | | 0.29 | 0.95 | 0.57 | 1.04 |
| | 1.52 | | 0.29 | 1.04 | 0.44 | 1.16 |
| | 1.54 | | 0.31 | 1.08 | 0.61 | 0.91 |
| | 2.3 | 0 | 0 | 0 | | 0 |
| | 2.3 | 0.2 | 0 | 0.16 | | 0.04 |
| | 2.3 | 0.6 | 0.11 | 0.48 | | 0.09 |
| | 2.3 | 1.2 | 0.21 | 0.78 | | 0.29 |
| | 2.3 | 1.8 | 0.27 | 0.99 | | 0.31 |
| | 2.3 | 2.3 | 0.32 | 1.01 | | 0.38 |
| | 2.3 | 2.3 | 0.36 | 1.05 | | |
| | 0.09 | | 0 | 0.04 | 0.05 | 0.04 |
| | 0.22 | | 0 | 0.20 | 0.12 | 0.11 |
| H-ZSM-5 | 0.38 | | 0 | 0.22 | 0.16 | 0.18 |
| | 0.60 | | 0 | 0.37 | 0.30 | 0.34 |
| | 0.69 | | 0 | 0.43 | 0.32 | 0.47 |
| | 1.01 | | 0.10 | 0.72 | 0.35 | 0.52 |
| | 1.20 | | 0 | 0.84 | | |

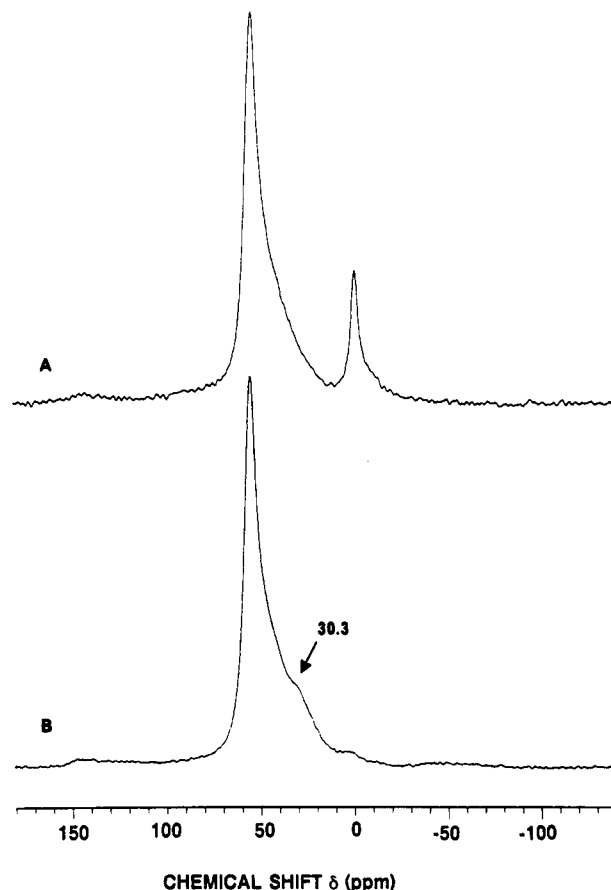
^a "[H⁺]" = [H⁺] + [ef.Al], as determined by conductometric titration. ^b "[H⁺]" = [H⁺] + [ef.Al], as determined by potentiometric titration. ^c Area of 3610-cm⁻¹ absorption band/area of 1870 cm⁻¹ absorption band.

**Figure 3.** Brønsted acidity (●) as determined by conductometric titration as a function of the aluminum content for H-ZSM-5.**TABLE II: Chemical Analysis for Si, Al, and Na, Consumption of OH⁻ as Determined by Conductometric Titration, and Amount of Extraframework Aluminum (ef.Al) of a Mordenite Sample before, during (Equivalence Point), and after Titration**

| | before | eq pt | after |
|---------------------|--------|-------|-------|
| Si/Al | 10.4 | 10.3 | 10.0 |
| Na ⁺ /Al | 0 | 0.74 | 0.81 |
| ef.Al/Al | 0.19 | 0 | 0 |
| OH ⁻ /Al | | 0.80 | |

extraframework aluminum species may contribute to the Brønsted acidity of the zeolite (eq 1), conductometric titration can be considered to afford a measure of the "total" Brønsted acid site concentration.

3. Correlation of IR Measurements with Conductometric Titration for H-Mordenite and H-ZSM-5 Zeolites. In order to substantiate the observations resulting from the conductometric titrations, acidity measurements were also performed using IR spectroscopy. The method employed comprised measurement of the area of the 3610-cm⁻¹ absorption of the zeolites, attributed to AlO-H vibrations of framework aluminum.^{32,33} Additionally, for the H-mordenite samples of fixed Al/variable H⁺ content,

**Figure 4.** ²⁷Al MAS NMR spectra of H-mordenite (1.52 mmol of Al/g) before (A) and after (B) conductometric titration.

the area of the 1545-cm⁻¹ absorption band of pyridine adsorbed on the zeolitic Brønsted sites was determined.³² It should be noted that, in all cases, adsorption of pyridine onto the samples resulted in the disappearance of the 3610-cm⁻¹ absorption, indicating that all the Brønsted sites had reacted. For both methods, the measured peak areas were corrected for the radiation path length of the samples³⁰ by dividing by the area of the 1870-cm⁻¹ band of the samples, the latter corresponding to a Si-O overtone of the zeolite framework.

The results of the IR measurements for the H-mordenite samples of fixed and varying aluminum content are collected in Tables I and III. Although the determination of the numbers of

TABLE III: Corrected Areas of the 1545- and 1455-cm⁻¹ Absorption Bands of Pyridine Adsorbed onto Mordenite Partially Exchanged with NH₄⁺ Prior to Calcination

| [NH ₄ ⁺], mmol/g | absorbance ^a | |
|---|-------------------------|-----------------------|
| | 1545 cm ⁻¹ | 1455 cm ⁻¹ |
| 0.0 (0) ^b | 0 | 0 |
| 0.2 (9) | 0.06 | 0.04 |
| 0.6 (26) | 0.17 | 0.19 |
| 1.2 (52) | 0.34 | 0.21 |
| 1.8 (78) | 0.39 | 0.21 |
| 2.3 (100) | 0.79 | 0.29 |

^a Absorbance: peak area of the absorption band normalized to the 1870-cm⁻¹ Si-O overtone absorption band. ^b In parentheses: NH₄⁺/Al molar ratio (%); mordenite samples contained 2.3 mmol of Al/g.

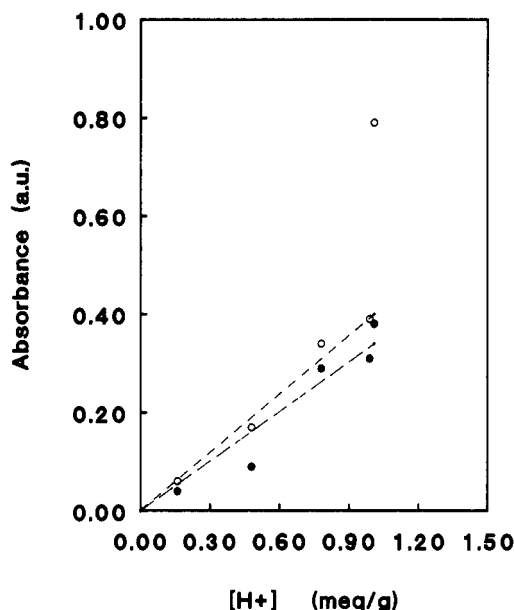


Figure 5. Area of the 3610-cm⁻¹ absorption band (●) and area of the 1545-cm⁻¹ absorption band (○) as a function of the concentration of Brønsted acid sites as determined by conductometric titration ("[H⁺]" = [H⁺] + [ef.Al]) for mordenite partially exchanged with NH₄⁺.

acid sites in the different zeolite samples is only relative using these IR techniques (since the relevant extinction coefficients are not known with any certainty), the results show reasonable agreement with those obtained by conductometric titration. Thus, the measured Brønsted acidity, in terms of the number of Al-OH groups, is only proportional to the framework aluminum concentration within the range 0–1.50 mmol/g, whereas at higher aluminum concentrations, the number of acid sites level off. The concordance between the results provided by the two techniques is emphasized by a plot of the corrected 3610- and 1545-cm⁻¹ peak areas against the corresponding number of Brønsted acid sites determined by conductometric titration (Figures 5 and 6), from which it emerges that (with the exception of one point in Figure 5, for which we have no explanation) a clear correlation exists for both the series of H-mordenites of fixed Al/varying H⁺ content and those of varying aluminum content. (Although, unlike IR, conductometric titrations effectively count extraframework aluminum as Brønsted sites, it should be remembered that the concentration of extraframework aluminum present is directly proportional to the total aluminum or NH₄⁺ concentration—hence the linear correlation between the two techniques.)

For the H-ZSM-5 samples studied, a linear correlation is found between the corrected areas of the 3610-cm⁻¹ peak and the framework aluminum concentration. Consequently, a plot of the 3610-cm⁻¹ peak areas against the corresponding concentrations of Brønsted acid sites determined by conductometric titration likewise affords a linear correlation (see Figure 6).

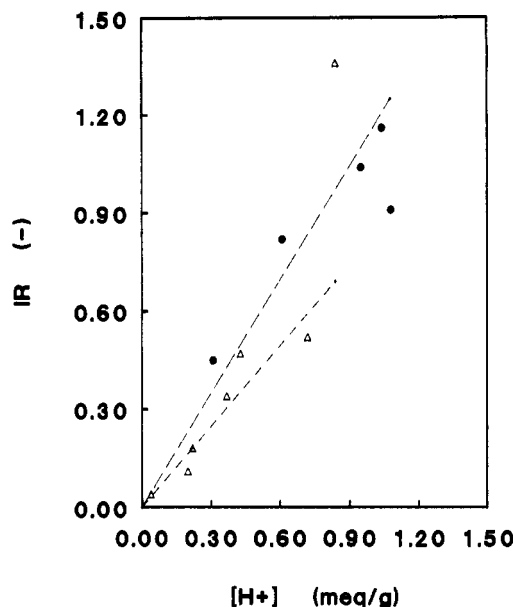


Figure 6. Area of the 3610-cm⁻¹ absorption band as a function of the concentration of Brønsted acid sites as determined by conductometric titration ("[H⁺]" = [H⁺] + [ef.Al]) for H-mordenite (●) and H-ZSM-5 (Δ) samples of varying Al content.

4. Discrepancy between Measured Brønsted Acidity and Framework Al Content. For both the ZSM-5 and mordenite zeolites studied in this work, an H⁺/Al ratio of less than unity could in principle be a consequence of (i) dealumination of the zeolite lattice and/or (ii) dehydroxylation of the lattice. These phenomena are discussed in the following paper⁸ and, therefore, are not considered further here. Additionally, there exists what at first sight may be regarded as a third possibility, specifically the existence of nonacidic Al-OH groups due to pairing of aluminum in the zeolite lattice.^{34,35} However, in the present work this explanation can be ruled out on the basis that (i) using IR spectroscopy all the Al-OH groups are counted and (ii) in a conductometric titration all the Al-OH groups are titrated. This latter point is born out by IR spectra obtained on the titrated zeolites, which show the complete disappearance of the 3610-cm⁻¹ absorption band for both the H-ZSM-5 samples and those H-mordenite samples with high aluminum content (see Figure 7).

5. Correlation of Potentiometric Titration with Conductometric Titration for H-Mordenite and H-ZSM-5 Zeolites. Aqueous techniques for the quantitative determination of Brønsted acidity in zeolites are generally based on potentiometric titration.^{4,11,36,37} In view of this, a comparative study was undertaken with the aim of assessing the relative advantages and disadvantages of conductometric and potentiometric titrations for this type of acidity measurement.

Potentiometric titrations were carried out on the series of H-mordenite and H-ZSM-5 samples varying in aluminum content which had previously been conductometrically titrated. In all cases, the potentiometric titrations were performed on the filtrates obtained by exchanging the zeolites with 3.4 M NaCl, following the procedure of Skeels and Flank.¹¹ Attempts to potentiometrically titrate the zeolite samples directly with NaOH were largely unsuccessful, end points being very poorly defined.

The results obtained using these two methods of acidity measurement are compared directly in Figures 8 and 9. The most striking feature of these results is the fact that potentiometric titrations consistently give lower values for the number of acid sites present. This finding may be rationalized on the basis that, in a conductometric titration, the accessible Brønsted acid sites are titrated according to the equation



whereas in an indirect potentiometric titration, only those protons

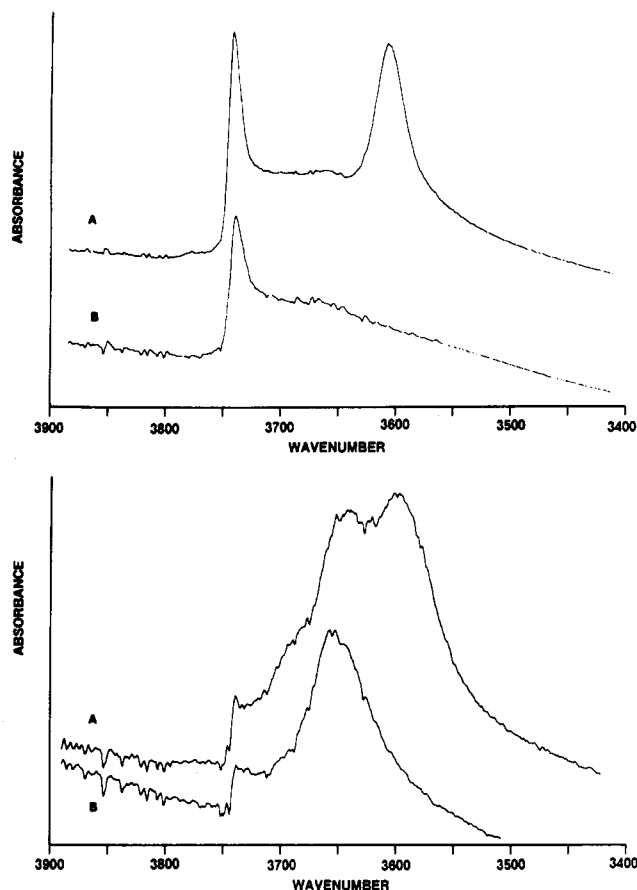


Figure 7. 3400–3900-cm⁻¹ region of the IR spectra of (top) H-ZSM-5 (0.60 mmol of Al/g) before (A) and after (B) conductometric titration and (bottom) H-mordenite (2.3 mmol of Al/g) before (A) and after (B) conductometric titration.

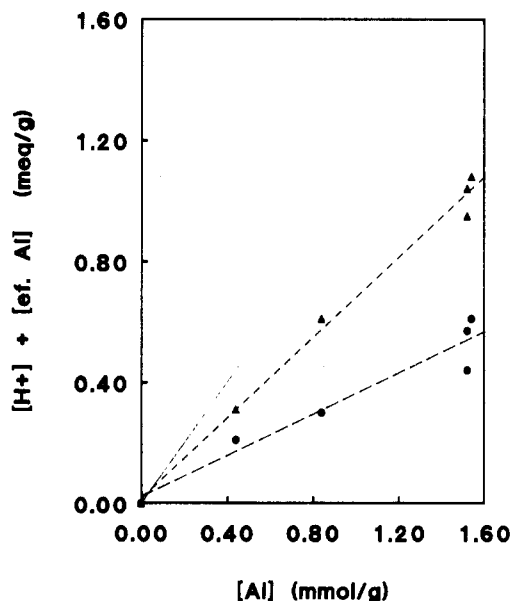


Figure 8. Brønsted acidity as determined by potentiometric (●) and conductometric (▲) titration as a function of the framework Al concentration for H-mordenite.

which can be exchanged out of the zeolite are titrated:



While the neutralization reaction depicted by eq 2 should go to completion (since titration is continued until past the equiv-

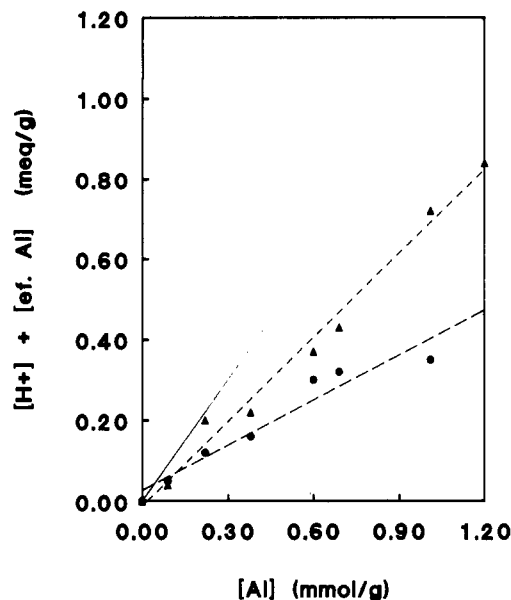


Figure 9. Brønsted acidity as determined by potentiometric (●) and conductometric (▲) titration as a function of the framework Al concentration for H-ZSM-5.

alence point), eq 3 represents an equilibrium process. From comparison of the conductometric and potentiometric titration results, it is evident that even when a large excess of NaCl is used for the ion-exchange reaction, the equilibrium in (3) does not lie completely to the right.

Verification of this is provided by IR and conductometric titration studies on the zeolite filter cakes isolated after the exchange reactions. In all cases, the exchanged zeolites are found to possess residual Brønsted acidity. Table IV shows results obtained from the conductometric titration of two Na⁺-exchanged protonic ZSM-5 samples. When the number of residual acid sites in the zeolite is added to the result of the potentiometric titration (on the filtrate), the number obtained in each case shows reasonably good agreement with the result obtained via direct conductometric titration of the protonic zeolite.

A potential advantage of the potentiometric technique is the fact that separate end points are obtained for the titration of H₃O⁺ and aluminum ions present, unlike the single end point observed for direct conductometric titrations. Thus, for H-mordenite samples shown by ²⁷Al NMR to contain extraframework aluminum, potentiometric titration likewise reveals the presence of (exchangeable) extraframework aluminum. In keeping with this, ²⁷Al NMR spectra obtained on the filter cakes of these zeolite samples after the exchange procedure showed in each case a relative decrease in the quantity of octahedral aluminum present of ca. 50%. However, once again, an equilibrium similar to that represented in eq 3 means that complete exchange of extraframework cationic aluminum species is unlikely. Demonstration of this is provided by the results of conductometric and potentiometric titrations performed on an Al-exchanged mordenite. As shown in Table IV, potentiometric titration yields a total number for the milliequivalents of aluminum and H₃O⁺ ions present (the latter being formed via hydrolysis of the aluminum ions), which is approximately half that determined using conductometric titration. The difference between these two figures is again accounted for by the presence of residual aluminum cations in the Na⁺-exchanged zeolite.

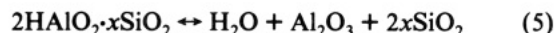
6. Limitations of Conductometric Titration and Related Aqueous Titration Techniques. Formerly, aqueous titration methods (based largely on potentiometry) were widely used for acidity measurements on amorphous silica–alumina cracking catalysts.⁴ However, a problem encountered in such measurements is the observation that titration of the solid in the aqueous phase frequently gives a value for the number of Brønsted acid

TABLE IV: Conductometric Titration of Filter Cakes Obtained from Indirect Potentiometric Titration of Selected Zeolites

| zeolite | pot. titn, mmol/g | filter cake, ^a mmol/g | total, ^b mmol/g | cond titn, mmol/g |
|---|-------------------|----------------------------------|----------------------------|-------------------|
| ZSM-5 (0.69 mmol Al/g) | 0.32 | 0.17 | 0.49 | 0.43 |
| ZSM-5 (0.38 mmol Al/g) | 0.16 | 0.10 | 0.26 | 0.22 |
| Al-mordenite ^{c,d} (0.16 mmol ef.Al/g) | 0.32 | 0.32 | 0.64 | 0.71 |

^a Determined by conductometric titration. ^b Total = filtrate (pot. titn) + filter cake (cond titn). ^c Titrated "[H⁺]" = [H⁺] + [ef.Al] (in mequiv/g). ^d [ef.Al] determined by elemental analysis; the substantial difference between measured "[H⁺]" and the ef.Al concentration reflects the presence of protons (formed by hydrolysis of Al³⁺ ions) introduced onto the exchange sites during preparation of the Al-mordenite.

sites which is greater than that obtained in anhydrous solvents. Oblad et al.³⁸ reported that, during the aqueous titration of silica-alumina catalysts with NaOH, the first end point was generally reached rather rapidly. After some hours, however, the pH of the suspension decreased, and a quantity of titer had to be added to reach the new end point. This observation was interpreted in terms of an equilibrium:



By neutralizing the acid aluminosilicate with the titrating base, the equilibrium would shift to the left, thereby creating more acidic sites. Additionally, the possibility is ever present that Brønsted sites can be formed from the reaction of water with incompletely coordinated aluminum ions (i.e., Lewis sites^{39,40}), a phenomenon which could also explain the excess acidity observed by Oblad et al.

Turning to zeolites, reactions of the type depicted in eq 5 are clearly unlikely in the absence of significant quantities of Al₂O₃. With regard to the conversion of Lewis sites into Brønsted sites, IR studies on X- and Y-type zeolites have shown that treatment of dehydroxylated samples with water can result in regeneration of some of the Brønsted sites.^{32,41} However, it is apparent that a distinction can be drawn between aluminum-rich zeolites such as zeolites X and Y and the more (hydro)thermally stable zeolites such as ZSM-5 and mordenite. Indeed, aqueous potentiometric titration has been successfully employed to demonstrate the increasing dehydroxylation that protonic ZSM-5 undergoes at progressively higher temperatures.¹¹ ZSM-5 samples, which according to thermogravimetric data had been fully dehydroxylated, were correspondingly found to possess negligible Brønsted acidity according to aqueous titration. These findings are in agreement with an earlier IR study, which also indicated that dehydroxylated ZSM-5 could not be rehydroxylated at room temperature.⁴² Similarly, an IR study of mordenite which had been dehydroxylated at 800 °C showed that hydroxyl groups were *not* re-formed on addition of water to the sample.⁴³

Our own observations are in accordance with these previous reports: pyridine adsorption/IR studies performed on H-ZSM-5 (1.01 mmol Al/g) and H-mordenite (0.84 mmol Al/g) zeolites prepared by in situ calcination of the ammonium zeolites reveal that there is no discernible change in the relative concentrations of Brønsted and Lewis acid sites after steam treatment of the zeolites (100 °C, 40 mbar, 1 h) (Figure 10). Together, these findings suggest that, in the case of ZSM-5 and mordenite, the extent of rehydroxylation resulting from the presence of water is (at room temperature) insignificant and that conductometric titration is therefore a valid analytical technique for these zeolites. In the case of X- and Y-type zeolites, this is probably not true; in any event, attempts to conductometrically titrate these latter zeolites are generally unsuccessful, with no clear end point being obtained.

Conclusions

For oxidic solids, it is known that aqueous titration procedures can be unreliable due to hydrolysis reactions which can alter the number of Brønsted acid sites present relative to those on the dehydrated surface. For ZSM-5 and mordenite zeolites, however, all the available data suggest that such reactions (and in particular the rehydroxylation of Lewis acid sites) do not occur at room

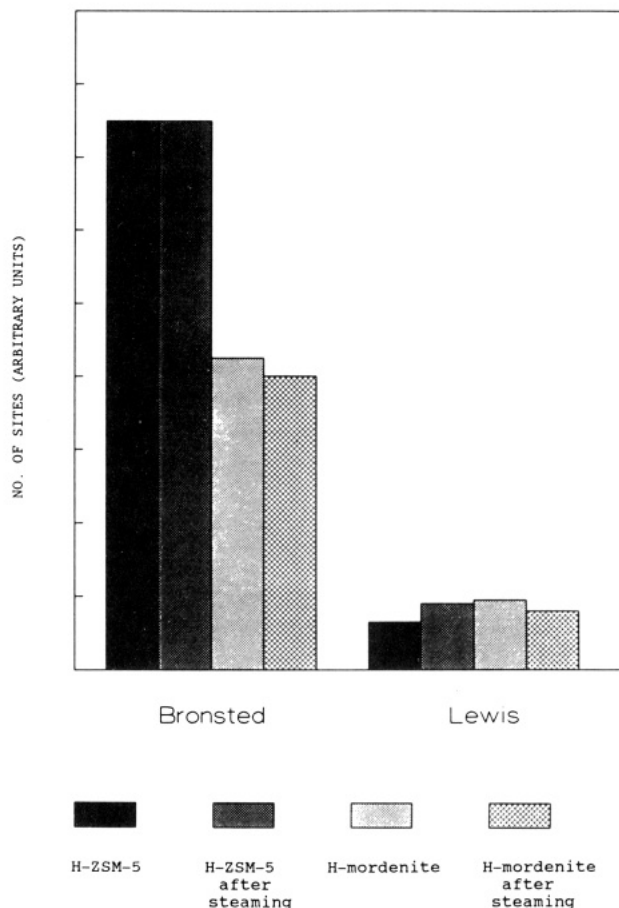


Figure 10. Relative concentrations of Brønsted and Lewis acid sites in H-ZSM-5 (1.01 mmol of Al/g) and H-mordenite (0.84 mmol/g) samples before and after steam treatment (as determined by pyridine adsorption/IR).

temperature. Furthermore, a good correlation has been observed between the results of acidity measurements made using conductometric titration and IR spectroscopy (area of the 3610-cm⁻¹ absorption band) on a series of H-ZSM-5 and H-mordenite zeolites with differing Si/Al ratio. We therefore conclude that conductometric titration is a reliable technique for the determination of Brønsted acidity in these zeolite types. The main weakness of the method lies in the fact that it measures only the total number of acid sites present and provides no information on the strength of those sites or the distribution of the acid site strengths. However, the quantitative nature of the technique, combined with the simplicity of its implementation, makes conductometric titration a useful supplement to the other existing techniques for acidity measurement in materials of this type.

Indirect potentiometric titration of ZSM-5 and mordenite zeolites affords values for the number of Brønsted acid sites present which are consistently lower than those obtained via direct conductometric titration. This observation may be explained by the fact that, in a conductometric titration, all the accessible Brønsted acid sites are directly titrated with base, whereas in an indirect potentiometric titration, only those protons (or aluminum cations) which can be exchanged out of the zeolite are titrated.

The numbers of Brønsted acid sites measured for H-ZSM-5 and H-mordenite zeolites using conductometric titration are consistently less than would be expected on the basis of aluminum content (typically around 70% of the theoretical value for H-ZSM-5), even after allowing for the presence of extraframework aluminum. This discrepancy may be attributable to dehydroxylation and/or dealumination of the zeolite samples during calcination.

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References and Notes

- (1) See, for example: (a) Maxwell, I. E. *J. Inclusion Phenom.* **1986**, *4*, 29. (b) Maxwell, I. E. *Catal. Today* **1987**, *1*, 385.
- (2) Kijenski, J.; Baiker, A. *Catal. Today* **1989**, *5*, 1.
- (3) Benesi, H. A.; Winkvist, B. H. C. *Adv. Catal.* **1979**, *27*, 97.
- (4) Forni, L. *Catal. Rev.* **1973**, *8*, 65.
- (5) Pfeifer, H. *Colloids Surf.* **1989**, *36*, 169.
- (6) Dwyer, J.; O'Malley, P. J. *Stud. Surf. Sci. Catal.* **1988**, *35*, 5.
- (7) See, for example: Low, P. F. *Soil Sci. Soc. Am. Proc.* **1955**, *19*, 135.
- (8) Sonnemans, M. H. W.; Den Heijer, C.; Crocker, M. J. *Phys. Chem.*, following paper in this issue.
- (9) Engelhardt, G. *Stud. Surf. Sci. Catal.* **1991**, *58*, 295.
- (10) Basset, J.; Denney, R. C.; Jeffery, G. H. *Vogel's Textbook of Quantitative Inorganic Analysis*, 4th ed.; Longman: London, 1978; Chapter XV.
- (11) Skeels, G. W.; Flank, W. H. In *Intrazeolite Chemistry*; Stucky, G. D., Dwyer, F. G., Eds.; ACS Symposium Series 218; American Chemical Society: Washington, DC, 1983; p 369.
- (12) Van Olphen, H. *J. Phys. Chem.* **1957**, *61*, 1276.
- (13) Higdon, W. T.; Marshall, C. E. *J. Phys. Chem.* **1958**, *62*, 1204.
- (14) Van Olphen, H.; Waxman, M. H. *Proc. 5th Natl. Conf. Clays Clay Minerals* **1958**, 61.
- (15) Gast, R. G.; East, P. J. *Proc. 12th Natl. Conf. Clays Clay Minerals* **1963**, 297.
- (16) Den Ouden, C. J. J.; Wielers, A. F. H.; Kuipers, H. P. C. E.; Vaarkamp, M.; Mackay, M.; Post, M. F. M. *Stud. Surf. Sci. Catal.* **1989**, *49B*, 825.
- (17) Sato, H.; Hirose, K.; Kitamura, M. *Nippon Kagaku Kaishi* **1989**, 1550.
- (18) Klyachko, A. L.; Mishin, I. V. *Pet. Chem. USSR (Engl. Transl.)* **1990**, *30*, 93.
- (19) Kühl, G. H. *J. Phys. Chem. Solids* **1977**, *38*, 1259.
- (20) Mirodatos, C.; Barthomeuf, D. *J. Chem. Soc., Chem. Commun.* **1981**, 39.
- (21) Zholobenko, V. L.; Kustov, L. M.; Kazansky, V. B.; Loeffler, E.; Lohse, U.; Oehlmann, G. *Zeolites* **1991**, *11*, 132.
- (22) Lohse, U.; Parltz, B.; Patzelová, V. *J. Phys. Chem.* **1989**, *93*, 3677.
- (23) Meyers, B. L.; Fleisch, T. H.; Ray, G. J.; Miller, J. T.; Hall, J. B. *J. Catal.* **1988**, *110*, 82.
- (24) Kürschner, U.; Jerschke, H.-G.; Schreier, E.; Völter, J. *Appl. Catal.* **1990**, *57*, 167.
- (25) Suzuki, K.; Sano, T.; Shoji, H.; Murakami, T.; Ikai, S.; Shin, S.; Hagiwara, H.; Takaya, H. *Chem. Lett.* **1987**, 1507.
- (26) Brunner, E.; Ernst, H.; Freude, D.; Hunger, M.; Krause, C. B.; Prager, D.; Reschetilowski, W.; Schwiager, W.; Bergk, K.-H. *Zeolites* **1989**, *9*, 282.
- (27) Brunner, E.; Ernst, H.; Freude, E.; Fröhlich, E.; Hunger, M.; Pfeifer, H. *Stud. Surf. Sci. Catal.* **1989**, *49A*, 623.
- (28) Reschetilowski, W.; Einicke, W.-D.; Jusek, M.; Schöllner, R.; Freude, D.; Hunger, M.; Klinowski, J. *J. Appl. Catal.* **1989**, *56*, L15.
- (29) Breck, D. W.; Skeels, G. W. In *Proceedings of the 5th International Conference on Zeolites*; Rees, L. V. C., Ed.; Heyden: London, 1980; p 335.
- (30) Goovaerts, F.; Vansant, E. F.; Philippaerts, J.; De Hulsters, P.; Gelan, J. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 3675.
- (31) Hays, G. R.; Van Erp, W. A.; Alma, N. C. M.; Couperus, P. A.; Huis, R.; Wilson, A. E. *Zeolites* **1984**, *4*, 377.
- (32) Ward, J. W. In *Zeolite Chemistry and Catalysts*; Rabo, J. A., Ed.; ACS Monograph No. 171; American Chemical Society: Washington, DC, 1976; p 118.
- (33) Jacobs, P. A.; Von Ballmoos, R. *J. Phys. Chem.* **1982**, *86*, 3050.
- (34) Barthomeuf, D. *Mater. Chem. Phys.* **1987**, *17*, 49.
- (35) Sawa, M.; Niwa, M.; Murakami, Y. *Zeolites* **1990**, *10*, 532.
- (36) Karge, H. G.; Dondur, V. *J. Phys. Chem.* **1990**, *94*, 765.
- (37) Martin, A.; Wolf, U.; Nowak, S.; Lucke, B. *Zeolites* **1991**, *11*, 85.
- (38) Oblad, A. G.; Milliken, T. H.; Mills, G. A. *Adv. Catal.* **1951**, *3*, 199.
- (39) Basila, M. R. *J. Phys. Chem.* **1962**, *66*, 2223.
- (40) Basila, M. R.; Kantner, T. R.; Rhee, K. H. *J. Phys. Chem.* **1964**, *68*, 3197.
- (41) Uytterhoeven, J. B.; Christner, L. G.; Hall, W. K. *J. Phys. Chem.* **1965**, *69*, 2117.
- (42) Vedrine, J. C.; Auroux, A.; Bolis, V.; Dejaifve, P.; Naccache, C.; Wierchowski, P.; Derouane, E. G.; Nagy, J. B.; Gilson, J.-P.; Van Hooft, J. H. C.; Van den Berg, J. P.; Wolthuizen, J. *J. Catal.* **1979**, *59*, 248.
- (43) Weeks, T. J.; Hilley, H. F.; Bolton, A. P. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2051.