

Study of the Dynamics of NH₃ Adsorption in ZSM-5 Zeolites and the Acidity of the Sorption Sites Using the Frequency-Response Technique

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The frequency response (FR) method has been applied to a study of the dynamics of NH₃ adsorption in various ZSM-5 zeolites. Rate spectra have been recorded with samples differing in crystallite size, Si-to-Al ratio, and cationic composition. The effect of temperature and ammonia pressure has been examined. Independent of sorbent composition and measurement conditions, either macropore diffusion or sorption was found to be the rate determining transport step. Diffusion control could be removed, leaving pure sorption rate spectra which have been used to characterize acid–base interactions. Under the quasi-equilibrium conditions of the measurements practically all of the sites examined are covered by the sorbate permitting rapid diffusional transport in the zeolitic micropores. The total and the relative amount of the different kinds of sites involved in the sorption processes have been shown to depend not only on sample characteristics but also on NH₃ pressure and temperature. Both the frequency and the intensity of the FR resonances vary if the sorption equilibrium conditions are varied, making the direct interpretation of the spectra difficult. Generally a slow and a fast process could be distinguished assignable to sorption on Brönsted and Lewis acid sites, respectively. The time constants of the parallel sorption processes were determined and correlated to the strength of the acid sites. Spectra determined for the H-forms are characteristic for the processes of (i) $\text{NH}_3 + \text{H}^+ \rightleftharpoons \text{NH}_4^+$ and (ii) $\text{NH}_4^+ + \text{NH}_3 \rightleftharpoons \text{NH}_3\text{--H}^+\text{--NH}_3$ equilibria. Under conditions where protonic acid sites are saturated with the sorbate, only process ii is detected with significant intensity. The FR method was found to be less sensitive in detecting the differences in the acidity of the weaker Lewis acid sites, such as Na⁺ and NH₄⁺ ions and positively charged extraframework Al species, but could be applied for characterizing the process of ammine complex formation over Cu–ZSM-5.

1. Introduction

Zeolitic solid acids are important catalysts used by the petroleum industry. The efficiency of these catalysts is largely determined by their acidity. The development of the theory of solid acids and bases, including zeolites, and also the methods used for measuring the acid–base properties have been widely reported.^{1–5} The chemisorption of a basic probe molecule has been studied by calorimetry, by temperature-programmed desorption (TPD), and by NMR, UV, and IR spectroscopies to obtain information on the concentration of acid sites and on their distribution by strength and type. However, the problem of completely describing the acidity of a solid have remained unresolved. A single calculation or measurement gives some insight into certain aspects only, but the simultaneous use of different characterization methods is often needed. The potential of the frequency-response (FR) technique for studying chemisorption kinetics has been known for some time, but relatively few studies have been devoted to adsorption on catalyst surfaces.^{6–17} Recently the use of the FR method was suggested for studying the chemisorption kinetics of ammonia, which is one of the bases most often used to probe zeolitic acidity.^{15–17} The FR and the kinetic characteristics of NH₃ sorption were

determined, and the parameters were considered useful in distinguishing the acidic sorption sites.

The kinetics of gas–solid interactions is often studied by relaxation methods. The frequency-response method is a relaxation method developed from the more simple transient-response (step or pulse) experiments. In these methods, the equilibrium of a system is instantaneously perturbed and the process of reestablishing the equilibrium is followed. In the case of the FR examination the perturbation is very small and periodic. Usually a pressure wave is generated by periodically changing the volume of a system containing the interacting gas and the solid which is in equilibrium. Frequencies of the periodic perturbation are chosen such that the process of reequilibration and the periodic modulation occurs on a comparable time scale. If the overall kinetics of a process involves several parallel steps, resonances appearing at different perturbation frequencies can be distinguished. The kinetic parameters of each different rate step can be deduced from the obtained perturbation frequency vs response function, by fitting the experimentally measured function with a function derived on the basis of an appropriate model, i.e., with a so-called characteristic FR function.^{6,7} Sorption and reaction on the surface are the last events of the process of gas–surface interaction comprising consecutive steps. These processes follow the diffusion of the gas molecules to the active solid surface. If inter- or intracrystalline diffusion determines the rate

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of the overall process, then diffusion can be studied by the FR technique.^{18,19}

The first attempts to apply the FR technique for characterizing the acid sites of zeolites were qualitatively promising, but the assignment of the FR signals to specific processes with various rates, such as intrazeolitic diffusion and/or chemisorption on sites of different acidity, remained speculative. The unsolved problem is the assignment of the processes of various rates to certain kinds of acid–base interactions, such as chemisorption on Brönsted and Lewis sites of different acidity.

The acidity of the ZSM-5 zeolites has been extensively studied.^{20–42} H-forms of different acidities could be obtained from the NH₄⁺-form of ZSM-5, depending on the conditions of the deammoniation treatment. If NH₃ release is paralleled with no or minor dehydroxylation, the preparation contains hydroxyl groups bridging between Si and Al atoms in an amount practically equivalent with the aluminum content.^{21,35–37} These hydroxyl groups located in the channel intersections are Brönsted acid sites.^{21,29} Different opinions were expressed about the energetic heterogeneity of these sites. Calorimetric studies suggest that sites are energetically homogeneous,^{35–37,42} but, on the basis of IR results, Datka and Tuznik²⁶ concluded that OH groups in different chemical environments must have different acid strengths. When dehydroxylation is allowed, or effected by steaming, aluminum is dislodged from the lattice and forms extraframework oxide species which can be of Lewis acid character. In interaction with the hydroxyls the Lewis acid sites enhance Brönsted acidity.^{22,23,27} As a result the acidity of a partially dehydroxylated ZSM-5 zeolite can be defined only with the distribution of sites by nature and strength. In acid treated samples the acid sites can show heterogeneity, not only in the acid strength but also in their location within a particle.²⁰

Part of the existing controversy about the acidic character of the various ZSM-5 preparations comes from the fact that the measured acidity is not only a function of the zeolite structure and composition but also depends on the properties and the amount of the basic probe used and on the conditions of the measurement, such as temperature.^{35,40} Furthermore, the value of the information obtained depends on the performance of the method used in distinguishing the different acid–probe interactions.

The objective of the present work was to gain a better understanding of the ammonia FR spectra by studying acidic ZSM-5 systems which are well-characterized by other techniques. Second, it is important to learn more about the dynamics of the sorption of ammonia and thereby about the acidity of ZSM-5, a zeolite which is a catalyst of great importance.

2. Experimental Section

2.1. Materials. ZSM-5 zeolites of different composition and morphology, synthesized and investigated in different laboratories, have been used as obtained or after modification treatment in this study. Parent ZSM-5 was modified by conventional ion exchange or by the method of solid-state ion exchange using the procedure suggested by Beyer et al.⁴³ The identification and the most important characteristics of the samples are given in Table 1.

The small crystallites of the Z23 sample (CAZ 49, Degussa, Germany) were intergrown to 100–200 μm aggregates; therefore, the sample was usually ground to a particle size smaller than 20 μm before the rate spectra of ammonia sorption was recorded. The rest of the samples were used without grinding in their original powder forms.

TABLE 1: Identification and Characterization of the ZSM-5 Samples

| sample ID | composn of the unit cell | av crystallite size, μm |
|--|---|-------------------------|
| Z15 ^a | | 3–10 |
| NH ₄ Z15 ^b | Na _{0.03} (NH ₄) _{5.77} Al _{5.8} Si _{90.2} O ₁₉₂ | |
| Na, NH ₄ Z15 ^c | Na _{3.83} (NH ₄) _{1.97} Al _{5.8} Si _{90.2} O ₁₉₂ | |
| NaZ15 ^d | Na _{5.8} Al _{5.8} Si _{90.2} O ₁₉₂ | |
| Cu NH ₄ Z15-99 ^e | Cu _{2.87} (NH ₄) _{0.06} Al _{5.8} Si _{90.2} O ₁₉₂ | |
| CuZ15-697 ^f | Cu _{20.2} Al _{5.8} Si _{90.2} O ₁₉₂ | |
| Z23 ^g | H _{3.91} Na _{0.16} Al _{4.06} Si _{91.6} O ₁₉₂ | 0.2–0.4 |
| Z34 ^h | H _{2.53} Na _{0.25} Al _{2.79} Si _{93.2} O ₁₉₂ | 3 × 4 × 7 |
| Z57 ⁱ | H _{1.6} Na _{0.06} Al _{1.6} Si _{94.4} O ₁₉₂ | 15 × 15 × 30 |

^a Parent sample obtained as a gift from the Zentralinstitut für Physikalische Chemie, Berlin, GDR. Si/Al = 15. ^b Sample was prepared from parent Z15. First template was burned off at 823 K, and then the template-free material was ion exchanged at 298 K using a 1 N aqueous solution of NH₄Cl. ^c Sample Na, NH₄Z15 was ion exchanged at 298 K using 0.2 N aqueous NaNO₃ solution. ^d The procedure given in ref 43 was followed. The powdered mixture of the Na,NH₄Z15 sample and NaCl was calcined in a vacuum at 823 K for 12 h. ^e Sample NH₄Z15 was ion exchanged at 298 K using 0.01 N copper acetate solution for 4 h. The exchange degree, 2[Cu]/[Al] × 100 = 99%. ^f Sample was obtained after a 35-day contact of the NH₄Z15 by a copious amount of 0.01 N copper acetate solution at 298 K. ^g The sample was provided by Degussa, Germany, with an identification CAZ 49. A detailed characterization of the sample is given in refs 17, 32, 33, and 37. A 47% amount of the total Al content is present in extraframework species. ^h The sample was provided by Degussa, Germany, with an identification CAZ 36. A detailed characterization of the sample is given in refs 17, 32, 33, and 37. A 25% amount of the total Al content is present in extraframework species. ⁱ The sample was synthesized at the Imperial College by Prof. S. Z. Chen in 1987.⁴⁴

The sorbate NH₃ was obtained from ARGO International with a purity of 99.96%.

2.2. FR Measurements. The FR apparatus used in the present work has been described previously.^{45,46}

About 50 mg of zeolite was placed into the chamber of the FR system and outgassed at 723 K for 1 h. As a result samples became dehydrated, and, by releasing ammonia, the NH₄⁺-forms were converted into the H-forms. Ammonia gas was admitted then to the pretreated sample, and the equilibrium was allowed to establish at about 0.4 or 1.0 Torr pressure. The effect of temperature was studied in the 273–823 K region.

The available frequency window was 0.01–10 Hz. The higher harmonic Fourier transformations of the square-wave response signals was used to extend the data points up to 90 Hz. The volume of the FR chamber was periodically modulated by ±1%. Under the same conditions measurements were carried out with zeolite (Z) and without sorbent (B). Phase-lag (Φ) and amplitude (P) were derived from equivalent fundamental sine-wave perturbations by a Fourier transformation of volume and pressure square waves. The phase-lag difference (Φ_{Z-B}) and the amplitude ratio (P_B/P_Z) were determined, and experimental FR functions were derived. The in-phase (δ_{in,real}) and the out-of-phase (δ_{out,imaginary}) components of FR functions generated theoretically are available for various gas/surface dynamic phenomena. The experimental and the corresponding theoretical functions for a simple gas–solid sorption system, according to the treatment of Yasuda,^{6,7} can be given by

$$(P_B/P_Z) \cos \Phi_{Z-B} - 1 = \sum (\kappa_j/\kappa_{-j})(\kappa_{-j}^2/(\kappa_{-j}^2 + \omega^2)) = \delta_{in,real} \quad (1)$$

$$(P_B/P_Z) \sin \Phi_{Z-B} = \sum (\kappa_j/\kappa_{-j})(\kappa_{-j}\omega/(\kappa_{-j}^2 + \omega^2)) = \delta_{out,imaginary} \quad (2)$$

In eqs 1 and 2

$$\kappa_j/\kappa_{-j} = (\delta A_j/\delta P)_e RT/V_e \quad (3)$$

where A_j is the amount of adspecies on the j sorption center, κ_{-j} is the time constant of the ad-/desorption process for adsorbate on the site j , and ω is the angular velocity of the wave generator. Subscript “e” denotes the equilibrium parameters. The in-phase function (δ_{in}) tends to κ_j/κ_{-j} in the lower frequency region. According to eq 3 parameter κ_j/κ_{-j} is in correlation with the equilibrium gradient of the adsorption isotherm. The maximum of the phase difference and that of the out-of-phase function (δ_{out}) appear at the perturbation frequencies of resonance, corresponding to the time constant of the transport. The $\delta_{out,imaginary}$ component plotted against the modulation frequency is often referred as the “rate spectrum” due to its similarities to spectroscopic examinations.

Intercrystalline mass or heat transfer resistance was found to be rate controlling if the sorbent formed even a shallow bed in the FR chamber. The size of the adsorbent particles was decreased by grinding, and particles were evenly dispersed in the sample holder. The same procedure is routinely applied in catalytic research when the kinetics of reactions is investigated. By dispersing on glasswool about 50 mg of a sample, the said transport barriers could be eliminated or could become unobservable in the frequency window applied. Working with the ammonia/zeolite system, the experimental conditions were selected such that only one of the consecutive steps of the intracrystalline diffusion and sorption process had to be considered as the likely rate controlling step responsible for the appearance of the resonance signal. The analysis of the results, vide infra, led to the conclusion that ammonia diffusion in the zeolitic micropores is not rate determining at the temperatures and pressures applied. The resonance frequencies, i.e., the frequencies of the steps (δ_{in}) and peaks (δ_{out}) in the spectra, were assigned to parallel sorption processes and used as parameters indirectly characteristic on the acidic sites involved in the ammonia sorption process.

The values of the associated dynamic parameters, κ_j/κ_{-j} and κ_{-j} of the ammonia sorption which are controlling the locations of the maximum of the out-of-phase function, were determined by fitting the experimentally obtained FR spectra with the characteristic FR functions as given by eqs 1 and 2.

2.3. IR Spectroscopic Measurements. Self-supporting pellets were prepared from the samples and were activated in situ in the IR cell by evacuation at 723 K for 3 h. The cell was made of quartz, equipped with an integral furnace and KBr windows. Pretreated pellets were cooled to room temperature moved between the windows, and a spectrum was recorded. Samples were contacted then with ammonia at 1 Torr pressure. Pellets were evacuated at 373 K and subsequently at 573 K for 30 min periods. A spectrum was recorded at 298 K after each evacuation treatment. A Nicolet 5PC FTIR spectrometer was used. A set of 500 scans was accumulated and averaged at a nominal resolution of 4 cm^{-1} . Absorbance was normalized to 5 mg cm^{-1} pellet thickness.

2.4. Isotherms of Ammonia Adsorption. Isotherms of adsorption were determined using an all-glass BET apparatus equipped with a Barocel Model 571A pressure transducer and Model 1174 electronic manometer.

3. Results

The ammonia interactions with the crystallite aggregates of the original sample Z23 and with the sample after grinding are

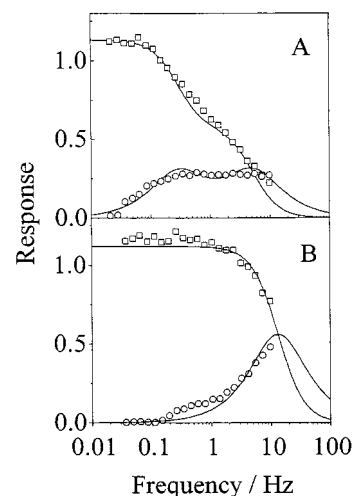


Figure 1. FR curves of ammonia for H-ZSM-5 samples of different particle size. Response curves were obtained at 373 K and 1 Torr NH_3 pressure using about 50 mg of sample Z23 (A) in original form containing 100–200 μm crystal aggregates, and (B) after grinding to 10–20 μm particles. Symbols \square , \circ denote experimentally determined in- and out-of-phase functions.

distinctly different. Invariant to the temperature of the measurement, two significant response peaks could be distinguished in the spectrum of the nonground sample but only a single peak was found in the spectrum of the ground sample. Representative data obtained at 373 K are shown in Figure 1A,B. It follows from the theory that the intensity of the FR spectrum is proportional to the gradient of the equilibrium adsorption isotherm. While the number of the peaks changed on grinding, the integrated intensity of the spectrum remained practically unaffected. The low-frequency signal, which could be eliminated by simply dispersing the ground powder within the FR sample chamber, can be assigned to a slower process, most probably to intercrystalline diffusion. It will be shown below that the high-frequency peak at about 10 Hz, belonging to a faster process, stems from the sorption of ammonia on acidic centers. According to the theoretical analysis of Reyes et al.⁴⁷ a coupled diffusion and sorption process can be decoupled by the FR method. However, the treatment given to the problem by Jordi and Do⁴⁸ suggests that the experimental data shown in Figure 1A cannot demonstrate a case when diffusion and sorption rates are comparable and the dynamics is controlled by diffusion at low and adsorption at high perturbation frequencies. The same result can be obtained if the size of the particles distributed in the FR chamber is inhomogeneous. Under such conditions intercrystalline diffusion can determine the rate in the large particles, while the sorption can be the rate controlling step in the small particles. When the limitation to intercrystalline diffusional transport was removed, the response function obtained became characteristic for pure adsorption (Figure 1B). The data clearly demonstrate that the FR technique can be selective for dynamic processes regardless of their nature. The objective of this work was to assign FR resonances to sorption of ammonia on acidic sites. Since it is rather difficult if spectra contain components from both diffusion and sorption, we devised our experiments to avoid diffusion control in the intercrystalline macropores.

The effect of temperature on the FR characteristics of sample Z34 is shown in Figure 2. As expected for a sample consisting of small and well-dispersed crystallites, only the high-frequency peak was observed. It follows from the theoretical analysis of the characteristic functions for adsorption–desorption processes that the δ_{out} function must intersect the δ_{in} function if adsorption

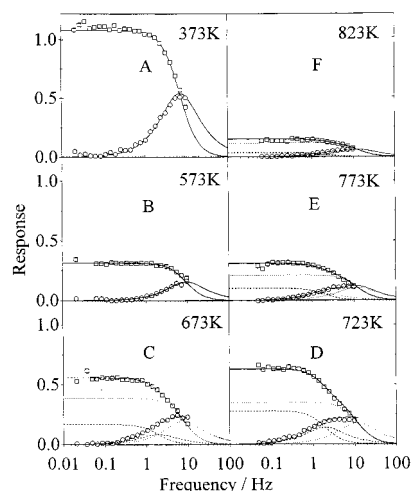


Figure 2. Effect of temperature on the ammonia FR curves of H-ZSM-5 zeolites. A 50 mg sample Z34 was used at 1 Torr ammonia pressure. Symbols \square , \circ represent the experimentally determined FR functions while lines correspond to the characteristic functions in accordance with eqs 1 and 2.

is rate determining. The point of intersection must be located at the maximum of the out-of-phase curve and at half of the maximum value of the steplike in-phase function. The relative form of the corresponding functions is distinctly different if diffusion is rate controlling. In this case the functions do not cross but approach zero asymptotically and concurrently at higher frequencies.^{6,7,47} The intersecting character of the functions in Figure 2 suggests that under the conditions of the measurements the diffusion is very fast relative to adsorption and the FR functions observed are characteristic therefore of adsorption. The integrated FR intensity of the δ_{out} function, $\Sigma(\kappa_j/\kappa_{-j})$, which is related to the gradient of the equilibrium ammonia adsorption isotherm according to eq 3, decreased as the temperature was increased. However, above 600 K an additional peak appeared at lower frequencies (Figure 2C–E). The intensity of this peak and, as a consequence, also the total intensity of the response signals grow with temperature in the 600–700 K range. However, above about 700 K the intensities start to drop again. The single resonance appearing at high and low temperatures (Figure 2A,F) suggest that at high and low NH₃ coverages ammonia sorption sites in H-ZSM-5 are energetically homogeneous. In contrast, at intermediate temperatures and coverages at least two distinctly different kinds of sorption centers participate in the ammonia sorption processes.

Integrated FR intensity vs temperature plots are given in Figure 3 for H-ZSM-5 samples of different Si/Al ratios. Similar forms for these temperature dependencies were found for all of the samples; however, the intensity was found to be smaller at any specific temperature for samples of higher Si-to-Al ratios. These results suggest that the total intensity corresponds to the aluminum content, which, on the other hand, is closely related to a number of acidic sites.

Adsorption isotherms of ammonia were determined up to 3.5 Torr pressure for sample Z34 at various temperatures (Figure 4). The gradient of these isotherms at 1 Torr and the $\Sigma(\kappa_j/\kappa_{-j})$ values plotted as a function of temperature are compared in Figure 3, where it is shown that the temperature dependence of the slope parallels that of the total FR intensity. Both functions pass through a minimum at about 600 K. For samples of different Si-to-Al ratios the FR spectra and parameters were determined at 723 K (Figure 5 and Table 2). Considering the

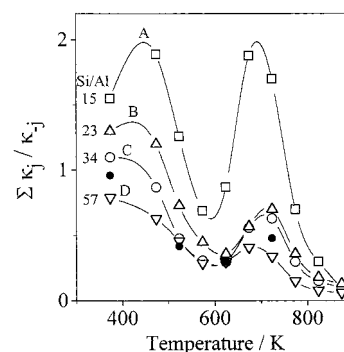


Figure 3. FR intensity vs temperature curves for H-ZSM-5 zeolites of different Si-to-Al ratios. About 50 mg samples of (A) Z15, (B) Z23, (C) Z34, and (D) Z57 was used at 1 Torr ammonia pressure. Symbol \bullet represents the value obtained as 5 times the gradient (in units of $\text{mmol s}^{-1} \text{Torr}^{-1}$) of the isotherms of sample Z34 at the same pressure.

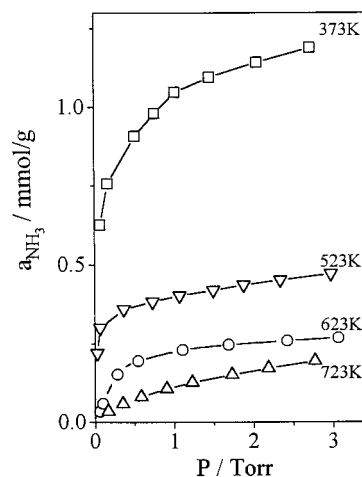


Figure 4. Isotherms of adsorption for ammonia on the H-ZSM-5 zeolite Z34. Sample was pretreated by 8 h evacuation at 723 K.

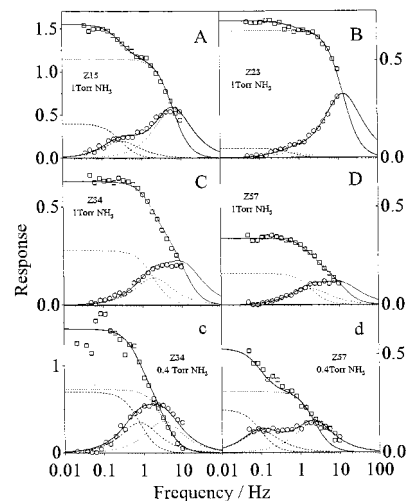


Figure 5. Effect of the Si-to-Al ratio on the ammonia FR curves of H-ZSM-5 zeolites. About 50 mg of sample (A) Z15, (B) Z23, (C, c) Z34, and (D, d) Z57 was used at 723 K and an equilibrium NH₃ pressure of (A–D) 1.0 and (c, d) 0.4 Torr.

results shown in Figure 2, a high-frequency and a low-frequency peak was expected to appear at this temperature. In general, the intensity of each peak increases with the Al content. The high-frequency peak ($j = 2$) of sample Z23 is a remarkable exception. Obviously the spectral differences cannot be accounted for simply by differences in the chemical composition. The samples compared were prepared by using various synthetic

TABLE 2: FR Parameters Obtained from the Fits of the NH₃ FR Curves Measured at 723 K on Different H-ZSM-5 Zeolites^a

| | | Si/Al ^b (p _e , ^c Torr) | | | | | |
|-------------------------------|---------|---|----------------|----------------|------------------|----------------|------------------|
| | | 15 (1 Torr) | 23 (1 Torr) | 34 (1 Torr) | 34 (0.4 Torr) | 57 (1 Torr) | 57 (0.4 Torr) |
| κ_{-j}^d | $j = 1$ | 2 | 4 | 12 | 5 | 12 | 0.6 |
| | $j = 2$ | 40 | 85 | 72 | 21 | 75 | 14 |
| κ_j/κ_{-j} | $j = 1$ | 0.40 | 0.05 | 0.28 | 0.70 | 0.16 | 0.22 |
| | $j = 2$ | 1.15 | 0.65 | 0.35 | 0.73 | 0.18 | 0.31 |
| $\Sigma \kappa_j/\kappa_{-j}$ | | 1.55 | 0.70 | 0.63 | 1.43 | 0.44 | 0.53 |

^a The experimentally determined FR curves and the best fits obtained using the characteristic functions for sorption are given in Figure 5.

^b For samples Z15, Z23, Z34, and Z57. ^c Equilibrium pressure. ^d Sorption time constant of species j .

routes and are therefore different not only in their compositions but also in their crystallite size and the concentration of extraframework alumina species. Numerous studies have demonstrated that extraframework alumina can have a significant effect on intracrystalline diffusivity and acidity (e.g., refs 22, 23, 26, and 27).

It can be theoretically and experimentally shown that the time constant for micropore diffusion within the zeolite crystallites and the corresponding FR resonance frequency of the process depends on the crystallite size only, provided that the zeolites are otherwise structurally and chemically identical.¹⁹ The FR parameters, κ_{-j} , given in Table 2 show that the resonance frequencies have no correlation with the crystallite size of the H-ZSM-5 zeolites studied; i.e., peaks appear at nearly the same frequency for samples of different average crystallite sizes (Z34 and Z57) or at different frequencies when the crystal size is about the same (Z15 and Z34). Thus, the crystallite size is not important in relation to the observed FR properties. This result is taken as additional evidence that resonances obtained can be interpreted as parallel sorption processes and there is no need to allow for the interference of micropore diffusion.

The comparison of Figure 5B,C suggests that the acidic sorption site associated with the low-frequency FR peak is present in a larger concentration in sample Z34 than in Z23. According to the bulk and framework compositions given in Table 1, a larger fraction of the lattice Al is charge-compensated by positively charged extraframework aluminum (EFAI) species in sample Z23 than in Z34. This suggests that the low-frequency FR peak is due to the interaction of the sorbate ammonia with the Brønsted acidic protons of the H-ZSM-5 zeolites. In sample Z23 only a few Brønsted protons are available for ammonia adsorption since some of the sites were removed by dealumination and some were neutralized by the extraframework alumina species.

FR spectra of samples Z34 and Z57 were recorded at two different NH₃ pressures (Figure 5 C, c and D,d). At the lower pressure the low-frequency peak was found to shift to lower frequencies. The shift is more pronounced for the higher-silica Z57 sample which had no extraframework aluminum.

The appearance of a response maximum at about 10 Hz is a common feature of the H-, Na-, and Cu-forms of the parent Z15 sample. The peaks at lower frequencies represent much slower processes (Figure 6). On increasing the temperature, the integrated intensities and the intensities of the lower-frequency peaks were differently influenced by the different cations present. The total intensities obtained for the H- and the Na-forms decreased, and some of the low-frequency peaks completely disappeared on raising the temperature. The response of the Cu-form was the opposite.

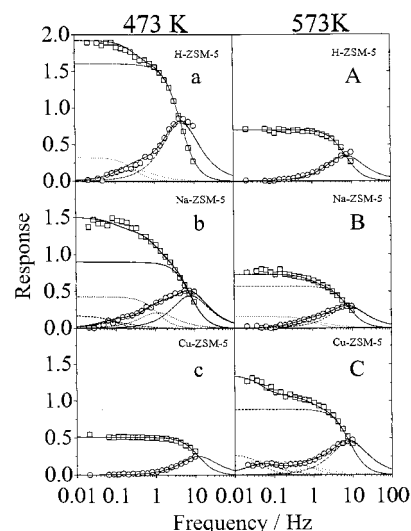


Figure 6. Ammonia response curves for ZSM-5 samples of different cationic forms. About 50 mg of sample Z15 was studied in (a,A) H-, (b,B) Na-, and (c,C) Cu-forms at 1 Torr NH₃ pressure at temperatures 473 K (a,b,c) and 573 K (A,B,C).

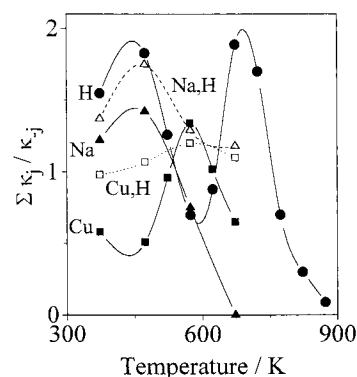


Figure 7. FR intensity of ammonia responses vs temperature curves for H- (●), Na- (▲), Na,H- (△), Cu- (■), and Cu,H-ZSM-5 (△) zeolites prepared from sample Z15.

The temperature dependence of the total FR intensity is compared for the different cationic forms of the Z15 sample in a broader temperature range in Figure 7. Above 673 K the FR spectrum of the Na-form was too weak, indicating little or no adsorption of ammonia. No spectra were recorded for the Cu-forms above 673 K because at these temperatures the copper ions were reduced by NH₃ to metallic particles as indicated by the appearance of a red sample color. Below about 550 K the temperature dependence of the integrated peak intensity follows the opposite trend to that of the H- and the Cu-forms. It is quite reasonable, therefore, to find that the FR intensity for the mixed ionic Cu-,H-form was practically independent of temperature. Such complex FR behavior seems very unlikely to come from rate controlling diffusion processes of NH₃ within the zeolitic pore system. It is more rational to assign each of the FR resonances obtained to a specific sorption interaction with a distinct time constant.

Recently a detailed MAS NMR and IR spectroscopic study was reported on the adsorption of ammonia on zeolites by Fripiat et al.⁴⁹ It was shown that, despite its strong basicity, ammonia can be used as a probe molecule to distinguish different Brønsted and Lewis sites. The IR results shown in Figure 8 are interpreted essentially on the basis of this work. The band observed at about 1630 cm⁻¹ can be assigned to the asymmetric deformation vibration of NH₃ (δ_{as} NH₃) adsorbed on electron acceptor sites. The coordinative binding to Lewis acid sites is

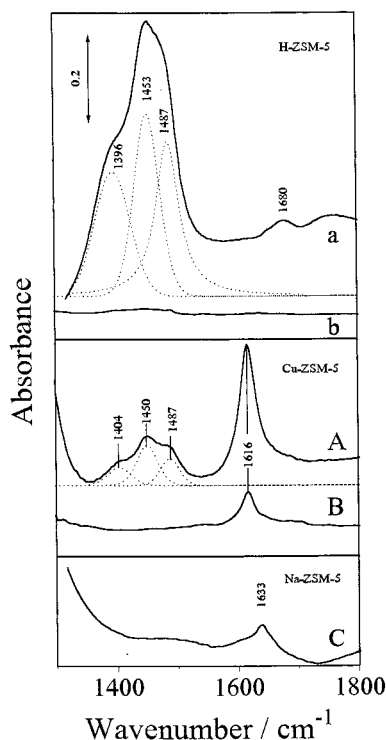


Figure 8. FTIR spectra of ammonia adsorbed on H- (a, b), Na- (C), and Cu-ZSM-5 (Z15) (A, B). Samples were evacuated at 723 K for 3 h, contacted with 1 Torr NH₃ at 298 K. Spectra were recorded at 298 K after 30 min evacuation at 373 K (a, A, C) and also after subsequent 30 min evacuation at 573 K (b, B).

the only form of adsorption of NH₃ on the Na-form of the Z15 sample (Figure 8C). Part of the adsorbed NH₃ is Lewis-bound on the H- and Cu-forms (Figure 8a,A). The Cu-form retained some of such species even after evacuation at 573 K, indicating that the binding of ammonia was much stronger on this than on the other cationic forms (Figure 8, spectrum B). Practically all of the adsorbed ammonia was removed from the Na-form, and most of it from the H-form by the same treatment (Figure 8b). These findings are in accordance with the observed temperature response of the total FR intensity of the samples (Figure 7). The difference in the binding strength is reflected in the somewhat different infrared δ_{as} NH₃ frequencies (1630 cm⁻¹ for the Na-form and 1616 cm⁻¹ for the Cu-form); however, this frequency is known to be rather insensitive to the electron acceptor character of the sorption site.

Using a curve-fitting computer program, component bands of the spectra were resolved from the spectrum of ammonia on the H- and the Cu-forms. The component bands found at about 1400, 1450, and 1680 cm⁻¹ stem from the deformation vibrations of two different NH₄⁺ species.⁴⁸ The additional band at about 1490 cm⁻¹ can be attributed to the δ_s (NH₃⁺) vibration of ammonia adsorbed on strong electron acceptor sites, such as incompletely coordinated Al³⁺ ions.

4. Discussion

The salient conclusion of the present study is that either macropore diffusion or sorption determines the rate of ammonia transport in the NH₃/ZSM-5 systems. Intercrystalline diffusion was the slowest transport process in aggregated crystallite particles or in shallow beds of small crystallites in the FR sample holder. These findings suggest that conclusions of earlier studies drawn about sorption or micropore diffusion based on FR data accumulated using pellets or a bed of the sorbent have to be

considered dubious. Figure 1 clearly demonstrates the effect of particle size distribution on the FR spectrum. One of the resonance peaks, that assigned to intercrystalline diffusion, was eliminated by grinding. The remaining δ_{out} peak (Figure 1B) and those FR peaks shown in Figures 2, 5, and 6 are attributed to a sorption process or parallel sorption processes. This assignment is supported by the intersection of the δ_{out} and δ_{in} component curves as predicted by calculation assuming rate controlling sorption.

Micropore diffusion was disregarded as a possible rate controlling mechanism since spectral characteristics could not be correlated with the crystallite size, but they could be successfully interpreted by those specific acid-base interactions which, as was demonstrated many times, are effective in ZSM-5 zeolites.

Explanation is required, however, about why the ammonia transport is rapid in the zeolitic micropores relative to the sorption. This problem can be best understood by considering the known concentration dependence of the self-diffusion coefficient. On the basis of their PFG NMR studies, Kärger and Pfeifer^{50,51} have shown that at low pressures NH₃ diffusivity rapidly increases with the NH₃ pressure. A strong interaction with the sorption sites poses energetic hindrance to the intracrystalline transport of the adsorbing molecules at low coverages, but at higher pressures the high-energy sorption sites are saturated by the sorbate and the interaction of the sorptive with the sites already holding sorbate and the sites left uncovered is much weaker. Transport within the pores becomes much more facile. Under the conditions of the FR experiments the sorption sites are virtually fully covered by the sorbate NH₃. Since diffusion limitation in the macropores was removed and FR conditions favor rapid micropore diffusion, the sorption becomes the rate controlling step for all of the samples under the conditions applied in this study. It should be noted, however, that the presence of large cations in narrow pores, such as K⁺ in zeolite A, can impose steric limitation to microporous NH₃ transport. Obviously, such steric hindrance cannot be removed by simply raising the NH₃ coverage. The examination of such systems is not covered in the present study.

Ammonia is a frequently used base for probing acid sites in TPD studies. As in FR experiments TPD examinations must also be designed such that slow diffusion in the macropores is not rate determining. If this requirement is satisfied, the problem with rate controlling micropore diffusion still remains. It follows from the nature of the TPD method that an acid site only releases ammonia when all of the less strongly bound NH₃ has been released. The transport of ammonia desorbing from the strongly acidic sites is much hindered in the zeolitic channels when these sorption sites are present in high concentration. Thus, it is not surprising that the rate of intracrystalline microporous diffusion of the desorbing NH₃ was found to control the rate of transport in H-ZSM-5 zeolites of high Si-to-Al ratios and useful information about acidity could not be obtained.^{34,52} In contrast, the FR method depends on the dynamics of all of the parallel sorption processes in the NH₃/zeolite system at a single temperature while the system is close to adsorption equilibrium and the probed sorption sites are practically fully covered. As a consequence, micropore diffusion is not usually rate controlling and information is obtained which is not necessarily available by TPD.

Frequency-response spectra are usually quite simple if diffusion is the rate determining step. Generally one characteristic peak is observed which can be attributed to the slowest consecutive macro- and micropore diffusion process involved.

In contrast the sorption rate spectra often consist of a number of overlapping peaks since parallel sorption processes of different rates can give resonance signals at different frequencies. Similarly to conventional spectroscopies one important aim of the present research is the assignment of the signals, i.e., to assign specific resonances to specific kinds of processes.

The important feature of the FR method is that the dynamics of the different sorption processes are scanned by changing the perturbation frequency while the state of the system is maintained close to adsorption equilibrium. Keeping this in mind, the results given in Figure 2 can be understood. In the adsorbed phase ammonia is populating the strongest available acid sites. While the pressure was the same, the coverage was changed by changing the temperature. At 673 K and above two δ_{out} peaks were resolved. The low-frequency peak can be assigned to processes related to adsorption and desorption of ammonia interacting with the zeolitic Brönsted acid sites. The sites are covered by NH_4^+ ions, and the equilibrium coverage is hardly disturbed during the measurement. These NH_4^+ ions are Lewis acid sites which, if no stronger acid is available, can also adsorb NH_3 . The high-frequency δ_{out} peak is attributed to the sorption of NH_3 on the NH_4^+ ions. The total intensity of the spectrum is related to the slope of the adsorption isotherm of ammonia at the equilibrium pressure (eq 3 and Figures 3 and 4), while the contribution of any specific process to the spectrum is related to the slope of the corresponding component adsorption isotherm. The Brönsted acid sites are fully covered at the lowest temperature of measurement, and coverage hardly changes with the perturbation of pressure. Accordingly the high-frequency resonance peak, stemming from the process of weak adsorption on the NH_4^+ ions is present. At the highest temperature the weak acid NH_4^+ ions have little participation in the NH_3 sorption. Thus, the peak detected is associated with sorption on the stronger Brönsted acid sites (Figure 2). The contribution of the two sorption processes to the total intensity changes with temperature. This is reflected in the characteristic total intensity vs temperature plots shown in Figure 3.

The results given in Figure 3 can be discussed in relation with the NH_3 TPD curves for H-ZSM-5. The TPD peak appearing at about 400 K was associated with physical or weak chemical adsorption, and the desorption maximum observed usually above 600 K was supposed to be due to the process of NH_4^+ decomposition ($\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$).²⁵ The same sites, namely, the strong Brönsted acid hydroxyl groups and the weak Lewis acid site NH_4^+ ions, must have been involved in the processes detected by the FR experiment resulting in the two maxima on the $\Sigma(\kappa_j/\kappa_{-j})$ vs T curves (Figure 3).

The FR spectra of Figure 5 shows that the acidic properties of ZSM-5 preparations of different compositions are distinctly different. The total intensity roughly follows the Si-to-Al ratio. The differences in the concentration of the extraframework aluminum (EFAI) can explain the deviations from a strict correspondence with composition. According to an earlier study³² samples Z23 and Z34 showed strikingly different catalytic properties in the MTG (methanol to gasoline) reaction. The Z23 containing about twice as much EFAI than Z34 showed favorable catalytic properties. It was also shown that most of the negative charge on the lattice of Z23 was balanced by positively charged EFAI species. The catalyst Z23 contained much stronger Brönsted acid sites than catalyst Z34, although in a much smaller concentration. The relative intensity of the high- and low-frequency resonances for the samples is in harmony with above conclusions. The time constant (κ_{-j}) or the intensity (κ_j/κ_{-j}) of the $j = 1$ resonance assigned to the

Brönsted acid sites is smaller for sample Z23 than for Z34, suggesting that Z23 contains a smaller number but stronger protonic acid sites (Figure 5 and Table 1). However, it should be noticed that correct comparison of the time constants and the absolute intensities would require that the relative coverage of the sites should be about the same. This is difficult to attain for samples of different composition. The strong pressure dependence of the FR characteristics clearly indicate that the influence of coverage factor cannot be neglected (Figure 5 and Table 1).

The assignment of the observed FR resonances of NH_3 sorption to sorption processes on weaker Lewis and stronger Brönsted acid sites is supported by the FR and IR results obtained for the different cationic forms. The ammonia is obviously more strongly bound to the protonic sites than to the weak Lewis acid Na^+ cations. With the sodium form only traces of residual Brönsted acid sorption sites can be detected (Figure 8). Accordingly the FR spectra for the Na-ZSM-5 shows an intense high-frequency peak at about 10 Hz and a much less intense one at lower frequencies (Figure 6b,B). It is interesting to note that the position of the high-frequency peak differs little among the different cationic forms (Figure 7).

Similar bands appear on the IR spectrum of ammonia adsorbed on Cu-ZSM-5 and on H-ZSM-5 (Figure 8, spectra A and a). The NH_4^+ ion has T_d symmetry and three IR active fundamental vibrations at 1685 (ν_1), 3134 (ν_2), and 1397 cm^{-1} (ν_4). In accordance with published results⁴⁹ the ν_4 band of the NH_4^+ ion, formed from ammonia by protonation on a Brönsted site of the ZSM-5 zeolite, was found to split into two bands. The component bands at about 1400 and 1450 cm^{-1} were suggested to belong to species formed on sites of different acid strengths. The low-frequency component was assigned to NH_4^+ generated on a stronger Brönsted acid site. It was substantiated that these sites are the bridging OH groups next to an isolated framework Al atom (with no Al in the second sphere). The high-frequency component band is associated with the rest of the bridging OH-groups.⁴⁹ In contrast with the IR results, the existence of two different Brönsted acid sites could not be substantiated by the FR method (Figures 2 and 5). A possible reason is the different resolution of the two methods. However, it must also be noted that the coverage of the sites during the two kinds of measurements was distinctly different. It must be realized that the acidity of the sorption sites decreases as the concentration of ammonia and thereby electron concentration on the framework increases. Minor differences in the acid strength of the sites may remain disguised under the quasi-equilibrium conditions of the FR measurements.

With the Cu-form the bands of Brönsted bound NH_3 probably develop from the interaction with protons generated during the dehydration by the heterolytic dissociation of water coordinated to the Cu^{2+} cations. The strong band at 1616 cm^{-1} is assigned to Lewis-bound ammonia. The position of this band is at a wavenumber 14 cm^{-1} lower than the corresponding band of the gas-phase NH_3 , indicating that the sorption interaction is strong. It is known that Cu-salts can form ammine complexes in aqueous solutions and some of these complexes, e.g., the Copper(II)-diammine chloride, are thermally stable up to 540 K. Cu^{2+} ammine complexes were shown to form also in Cu-ZSM-5.^{53,54} Therefore, the binding of NH_3 should be stronger to Cu^{2+} than to Na^+ or NH_4^+ . When the temperature is increased, the NH_3 coverage decreases and the contribution of the processes involving stronger sorption interactions, if any, contribute more and more significantly to developing the FR spectrum. These interactions can bring about an increase in

the total FR intensity at higher temperatures (Figures 3 and 7). The monotonically decreasing $\sum \kappa_j / \kappa_{-j}$ vs T plot obtained for Na-ZSM-5 suggests that a single kind of sorption process is dominating over the whole of the temperature range examined. Obviously various temperature dependencies can occur with mixed cationic forms (Figure 7).

5. Conclusions

The dynamics of the ad-/desorption processes can be characterized by the FR method. The FR method has the advantages over other techniques that it is sensitive to the rate controlling process step and can selectively distinguish the different processes. Under the quasi-equilibrium conditions of the FR measurements either sorption or macropore diffusion was found to be the rate determining process for the ammonia/ZSM-5 systems. On the basis of the observed change of the FR response with temperature, pressure, and ZSM-5 composition, ammonia sorption on Lewis and Brønsted acid sites, as well as processes involving Cu-ZSM-5/ammine complexes could be distinguished.

The FR technique can be used to measure the ad-/desorption kinetics of ammonia probe molecule and for characterizing the acid sites. The combination of the conventional methods, such as TPD, IR, and NMR, with the FR method can lead to a more complete characterization of acid-base interactions.

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