Interaction of NH$_3$ with Brønsted acid sites in different cages of zeolite Y as studied by $^1$H MAS NMR

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Interaction of NH₃ with Brønsted Acid Sites in Different Cages of Zeolite Y As Studied by ¹H MAS NMR

W. P. J. H. Jacobs, J. W. de Haan, L. J. M. van de Ven, and R. A. van Santen

Schuit Institute of Catalysis, Laboratory of Inorganic Chemistry and Catalysis, and Laboratory of Instrumental Analysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

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Ammonia adsorption onto acidic zeolites is studied with ¹H MAS NMR (at 295–320 K). The influence of the amount of adsorbed ammonia is investigated in the presence of sodium or cesium as exchangeable cations and for different framework compositions (Si/Al = 2.4–12). The Brønsted sites in unloaded or partially loaded zeolites are observed near δ = 3.9 for protons in supercages and near δ = 4.6 for protons in sodalite cages. Ammonium ions under condition of no proton-exchange resonate at δ = 8.1. These species are detected as such only in the sodalite cages. In the supercages, a signal at δ = 6.9 is observed, which is assigned to an exchange involving NH₄⁺ (δ = 8.1), H⁺ (δ = 3.9), and NH₃ (δ = 0.8). Furthermore, in the sodalite cages, a signal at δ = 6.5 is observed, which is assigned to an exchange involving NH₄⁺ (δ = 8.1), H⁺ (δ = 4.6), and NH₃ (δ = 0.8), but with different relative residence times. Additionally, ammonium-ammonia signals are found at δ = 5.3–5.9 and at a position determined by the NH₃/NH₄⁺ ratio in the zeolite (δ = 7–1). For the ammonium-ammonia species proton-exchange between ammonium and ammonia is fast compared to the time scale of the NMR experiment. For at least two ammonium species proton-exchange with the Brønsted protons is fast, and consequently the lines are shifted to δ = 6.9 and 6.5. This implies that ammonium ions observed at δ = 8.1 have the lowest basicity and the ammonium ions at δ = 6.5 have the highest basicity. However, for the temperature range used, ammonia reacts statistically with the Brønsted sites of different acid strength.

Introduction

The proton form of zeolite Y is used as a catalyst in hydrocarbon processing. This solid acid is usually obtained from the ammonium-exchanged form, after desorbing ammonia and water at elevated temperatures. Ammonia adsorption onto the proton form or the reverse process, ammonia desorption at elevated temperatures, is used to characterize the acidity of the solid acid. This can be done, e.g., with temperature programmed desorption (TPD) techniques or with microcalorimetric measurements. In order to understand the experimentally obtained results at an atomic level, quantum chemical calculations are performed. From these calculations information is obtained about the geometry of the Brønsted sites in terms of bond lengths and bond angles. Further, the energies involved in transferring the proton to the ammonia molecule are calculated, and the geometry of the ammonium ion with respect to the lattice is predicted. So, ammonia adsorption onto the zeolitic structure is an interesting subject, both for experimental and for theoretical studies of zeolite acidity.

Spectroscopic techniques are extensively used to study these phenomena. With infrared spectroscopy two bands are observed for zeolite Y, which are due to the hydroxyl stretching modes of different Brønsted sites. The high-frequency band near 3645 cm⁻¹ (HF-OH) is assigned to the hydroxyl groups pointing into the supercages, involving the O₁ atoms. The hydrogen atoms at O₂ and O₃ in the sodalite cages cause the low-frequency band near 3550 cm⁻¹ (LF-OH). Both infrared bands decrease in intensity after adsorption of ammonia, and the formation of ammonium ions is shown by the appearance of the N–H deformation modes of ammonium ions near 1450 and 1670 cm⁻¹ and also by the ammonium lattice vibrations near 160 cm⁻¹. From far-infrared experiments it was concluded that the ammonium ions can be located at different cation sites, e.g., sites 1', 11, and 111 (see Figure 1).
TABLE I: Samples and Compositions Loading with Ammonia, and Observed NMR Lines at a MAS Frequency of 9 kHz

<table>
<thead>
<tr>
<th>samples</th>
<th>loading of NH3/unit cell</th>
<th>chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O–H</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(signals: (sh) shoulder, (w) weak, (vw) very weak)</td>
</tr>
<tr>
<td>no.</td>
<td>composition*</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Na4(NH4)NO3–Y (Si/Al = 2.8)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51</td>
</tr>
<tr>
<td>2</td>
<td>Na2(NH4)22–Y (Si/Al = 2.8)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>(NH4)351–Y (Si/Al = 2.8)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
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<td>95</td>
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<td></td>
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<td></td>
<td>11.2</td>
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<tr>
<td></td>
<td></td>
<td>95</td>
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<td>5</td>
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<tr>
<td></td>
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<td>4.5</td>
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<td></td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>6</td>
<td>Na51–Y (Si/Al = 2.8)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>NH4–Y (Si/Al = 5)</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
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<td>2.7</td>
</tr>
<tr>
<td></td>
<td>excess*</td>
<td>2.1</td>
</tr>
<tr>
<td>8</td>
<td>NH4–Y (Si/Al = 12)</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>26</td>
</tr>
</tbody>
</table>

* According to chemical analysis and 29Si MAS NMR. \( ^{4}H \) Excess ammonia adsorbed at room temperature onto the proton form, followed by evacuation at room temperature.

due to hydroxyl groups of extralattice aluminium derivatives. When excess ammonia is adsorbed compared to the acidic sites in the zeolites, additional signals can be found near \( \delta = 5.3 \) and at a position determined by the loading with ammonia (\( \delta = 7-0 \)) \(^{23-26} \). These signals are due to ammonium ions in fast proton exchange with ammonia. Recently, the spinning sidebands belonging to the Bronsted sites have been studied and interpreted in terms of dipolar interactions between \( ^{1}H \) and \( ^{27}Al \) nuclei. In this way the \( H–Al \) distances and the chemical shift anisotropies of the acidic hydroxyls are calculated. \(^{24-26} \) The interaction of ammonia with Bronsted sites has been studied for zeolite rho by Vega and co-workers. \(^{27} \) They showed, using \( ^{29}Si \) (CP) MAS NMR, that for the anhydrous zeolites the acidic protons and the ammonium ions are more rigidly bonded to the lattice than in the hydrated zeolites. Whereas in the anhydrous protonic sample the \( ^{1}H–^{27}Al \) dipolar interactions are dominant, in the samples with ammonium anhydrous ammonium the \( ^{1}H–^{1}H \) dipolar interactions in the same ion are of main importance.

Michel and co-workers \(^{28,29} \) used conventional Fourier transform \( ^{15}N \) NMR to study the adsorption of ammonia onto zeolites. More recently, Earl and co-workers \(^{30} \) studied the adsorption of ammonia onto zeolite Y using \( ^{15}N \) (CP) MAS NMR. They observed two different ammonium species with different mobilities. Chemical exchange or isotropic diffusion are so slow for these species that cross-polarization of \( ^{15}N \) with \( ^{1}H \) is possible. At high loadings with ammonia the ammonium ions interact with the ammonia molecules via hydrogen bonding, giving rise to additional features in the \( ^{15}N \) MAS NMR spectra. The excessive ammonia molecules in the zeolite are quite mobile, and they give rise to a broad chemical shift dispersion.

In this work we will use \( ^{1}H \) MAS NMR to study the interactions of ammonia and acid sites in the different cavities of zeolite Y, with the aim of gathering additional information regarding the interaction of the acid sites with probe molecules and the relative accessibilities of the different types of cages. More in particular we will pay attention to the partition of ammonia over different sites at low loadings and the possibly different behavior of ammonia when forced predominantly into one of the cages.

Solvation is one of the factors which determine the acid strength. The solvent is one of the factors which determine the acid strength. The solvation of the ammonium ions by the faujasite lattice will be briefly mentioned.

Experimental Section

The samples used are listed in Table I. Samples 1 and 2 were obtained by exchanging 18 g of sample 6 (Na43–Y: Akzo PA42611B, Si/Al = 2.8) at room temperature in 900 mL of 0.1 M nitrate solutions, containing ammonium and sodium ions in the ratios 0.32:1 and 4.3:1, respectively. The completely exchanged sample 3 was obtained after 9-fold exchange with 1 M solutions of NH4NO3 at 353 K. Sample 5 was obtained after 4-fold exchange at 353 K of sample 4 (Linde LZ-Y62, Si/Al = 2.4) in 1 M solutions of NH4NO3, followed by 3-fold exchange at room temperature in 0.3 M solutions of CsCl. Two dealuminated Y zeolites (samples 7 and 8) were prepared by dealuminating Na51–Y with SiCl4 at 523 K for 15 or 60 min. \(^{31-34} \) After being washed with demineralized water, the samples were converted to the ammonium forms by 4-fold exchange at 353 K in 2 M solutions of NH4NO3. The compositions of the samples as listed in Table I are obtained from elemental analyses on sodium, silicon, aluminium, and cesium. The Si/Al rations of the framework were determined from \( ^{29}Si \) MAS NMR experiments. According to X-ray diffraction (XRD), all samples were highly accessible of the different types of cages. More in particular we will pay attention to the partition of ammonia over different sites at low loadings and the possibly different behavior of ammonia when forced predominantly into one of the cages. Solvation is one of the factors which determine the acid strength. The solvation of the ammonium ions by the faujasite lattice will be briefly mentioned.
being degassed for 3 h, the samples were cooled to room temperature. The pressure was now less than 10^-3 Pa. Anhydrous ammonia (UCAR, 99.997% purity) was subsequently adsorbed on part of the samples; the amount adsorbed was determined volumetrically. Coverages with ammonia ranging between 0.07 and 6.4 times the number of Brønsted sites were applied. Finally, the ampules were sealed. The samples were transferred from the ampules to 4-mm ZrO2 MAS rotors of standard Bruker design under an inert nitrogen atmosphere and sealed with the spinner caps. Duration experiments indicated that no spectral changes occurred after several days, indicating that water uptake or ammonia desorption was negligible. The treatment of the samples did not result in severe structural damages, since the 1H MAS NMR experiments revealed only very weak signals due to silanol groups or hydroxyl groups of extralattice aluminium derivatives for the nondealuminated zeolites. This is further supported by 27Al MAS NMR experiments, which were performed using the samples before treatment and after adsorption of excessive amounts of ammonia. These spectra were recorded on a Bruker MSL 400 spectrometer by co-adding 1000 free induction decays (FID’s) using single 25° pulses with repetition times t1 = 1 s at a sample spinning frequency of 10 kHz. For the nondealuminated zeolites in all cases a strong signal due to tetrahedrally coordinated aluminium was observed, whereas the contribution due to octahedrally coordinated aluminium was less than 0.5%. In the dealuminated samples the amount of octahedrally coordinated aluminium was approximately 5–10%. After re-adsorption of ammonia a slightly lower amount was found. This may be due to the heating procedures used.

The 1H MAS NMR spectra were obtained at 300 MHz (7.0 T) on a Bruker CXP 300 spectrometer or at 400 MHz (9.4 T) on a Bruker MSL 400 spectrometer, both with a standard double-air-bearing MAS probe. Experiments were carried out at 295 and 320 K. Spectra were obtained for stationary samples and for samples spinning at frequencies from 1 to 9 kHz. Sixteen to forty FID’s were accumulated by using single 50° pulses (t1 = 1 μs) with repetition time t2 = 60 s and spectral width SW = 40 kHz. For samples saturated with ammonia, shorter repetition times (t2 = 5 s) could be used.

Infrared spectra of the zeolites in the proton forms were recorded in transmission mode on a Bruker IFS 113v FTIR spectrometer equipped with a heated vacuum cell. Self-supported discs were used for the measurements. The samples were pretreated in the cell for 1 h at 723 K before the room temperature spectra were recorded.

Results and Discussion

Brønsted Signals. In Table I the observed NMR lines for all experiments are summarized. After samples 1–4 were heated, a NMR signal near δ = 3.9 is observed (Figures 2–4). With increasing proton concentration of the samples, a shoulder near δ = 4.6 develops. For sample 5 (Figure 4) a signal near δ = 4.7, with a shoulder at δ = 3.4, is observed. The intensities for the various signals correlate with the intensities for the infrared stretching modes of the Brønsted sites (Figure 5). At low proton concentration only the high-frequency hydroxyl (HF-0H) band is observed, and only at higher proton concentrations the low-frequency hydroxyl (LF-0H) band develops. Sample 5 shows mainly the LF-0H band since the large cesium ions cannot penetrate into the sodalite cages, whereas the ammonium ions, which produce the acidic protons, can. So the signal near δ = 3.9 corresponds to the infrared HF-0H band, which is related to protons bonded to 02 and pointing into the supercages. These protons are bonded to 03 or 02. The protons on 02 or 03 are located near the oxygen atoms of the hexagonal prism. The others, localized at 02, point into the six-ring window between the sodalite cages and the supercage. The protons on 02 or 03 both have two close oxygen neighbors at 2.6 Å in the same six-ring. Due to the presence of these oxygen atoms, the infrared stretching mode is shifted to lower wavenumbers and the NMR line is observed at lower field. For the dealuminated samples (see Table I), the band maximum (δ = 4.0) is slightly shifted to lower field. This is in agreement with the results obtained by Freude and co-workers, who also found a shift to lower field with increasing Si/Al ratio. Similar to the nondealuminated zeolites, a shoulder is observed at δ = 4.6, which becomes better resolved by increasing the MAS frequency from 9 to 14 kHz. Additionally, only for the dealuminated zeolites a broad but low signal near δ = 2.7 is observed due to lattice imperfections (e.g., hydroxyl groups at extraframework aluminium). These protons are non-acidic, since they do not react with ammonia. Brunner has investigated the line broadening mechanisms for the lines due to the Brønsted sites in the 1H MAS NMR spectra. It was concluded that at high spinning rates (more than ca. 10 kHz) and at fields from 7.0 to 11.7 T the main contribution comes from the dispersion

![Figure 2](image-url) Room temperature 1H MAS NMR spectrum (at 9.4 T) of sample 1 at a MAS frequency of 9 kHz: (a) unloaded sample; (b) 3.6 molecules of NH3 adsorbed/unit cell.

![Figure 3](image-url) Room temperature 1H MAS NMR spectrum (at 9.4 T) of sample 3 at a MAS frequency of 9 kHz: (a) unloaded sample; (b) 3.6 molecules of NH3 adsorbed/unit cell; (c) 10.2 molecules of NH3 adsorbed/unit cell.
interaction of NH₃ with Brønsted Acid Sites


Figure 4. Room temperature ¹H MAS NMR spectrum (at 9.4 T) of sample 5 at a MAS frequency of 9 kHz: (a) unloaded sample; (b) 4.5 molecules of NH₃ adsorbed/unit cell; (c) 9.7 molecules of NH₃ adsorbed/unit cell.

Figure 5. Room temperature infrared spectra after 1-h evacuation at 723 K of sample 1 (a), sample 2 (b), sample 3 (c), and sample 5 (d). The decreases in intensities of the maximum at δ = 3.9 and of the shoulder at δ = 4.6 are the same within the experimental error. Freude and co-workers found that pyridine interacts preferentially with the acidic protons in the supercages, responsible for the line at δ = 3.9. Infrared experiments showed that carbon monoxide also reacts preferentially with the acidic protons in the supercages.

The ammonia molecule is much smaller than pyridine and can penetrate the zeolite six rings and hence react with the Brønsted sites in the sodalite cages. Ammonia is a much stronger base than carbon monoxide. So for ammonia adsorption at room temperature the energy gain is mainly determined by the protonation energy of the ammonia molecule, whereas differences in acidity of the Brønsted sites are smaller and of minor importance. The interaction energy of carbon monoxide with the Brønsted sites is much weaker, and now differences in acidity of the various sites become important. Since the protons at O₂ and O₃ (δ = 4.6, LF-OH infrared band) have two close oxygen neighbors at 2.6 Å, this interaction is probably energetically favorable enough to prevent adsorption of carbon monoxide at these sites. On the other hand, Hoffman and co-workers concluded from temperature programmed desorption experiments that the hydroxyls in the supercages are the most acidic. However, these results are obtained at temperatures exceeding 450 K. At low temperature the adsorbed ammonia has probably reacted statistically with the available acidic sites, whereas at high temperatures equilibrium is obtained between sites with different acidic strengths.

Ammonium Signals. After adsorption of small amounts of ammonia an NMR signal due to ammonium ions is observed at δ = 6.9 for samples 1–4. For sample 3 this signal has a weak shoulder at lower field. At low loadings with ammonia this shoulder is observed near δ = 7.0–7.5. At excess loadings (Figures 6–8) all available acidic sites are covered with ammonia. The shoulder for sample 3 develops into a weak signal, which is shifted up to δ = 8.1 (Figure 6). The intensity of this signal corresponds only to a few ammonium ions per unit cell.

At low loadings for sample 5 a strong line is observed at δ = 8.1, with a small shoulder near δ = 7.1 (Figure 4). At excess loadings the shoulder has disappeared (Figure 8). Also, we observe now that with increasing loading the intensity for the line at δ = 8.1 decreases from approximately 18 ammonium ions/unit cell (which is the amount expected at saturation of all acidic sites) to approximately 3 ammonium ions/unit cell for the highest loading applied onto this sample.

For the samples containing no or only a few residual sodium cations (samples 3 and 4) the line previously observed at δ = 6.9 is shifted to δ = 6.5 at excess loadings and has then a much smaller line width (see also Figures 9 and 10). For sample 3 this line corresponds to approximately 16 ammonium ions/unit cell for bulk NH₃/NH₄⁺ ratios between 0.3 and 1.0. (In the calculations of the NH₃/NH₄⁺ ratios we assume that each Brønsted site reacts with an ammonia molecule under the formation of an ammonium ion.) For sample 4 this signal corresponds to approximately 5 ammonium ions/unit cell at a bulk NH₃/NH₄⁺ ratio of 1.0 (Figure 10). Hence, the presence of this line is related to the degree of ammonium exchange of the samples. When the sodium content is moderate, the residual
sodium cations are located at sites I' in the sodalite cages, and some sodium cations remain at sites II in the supercages after the ammonium exchange. At increasing degrees of ammonium exchange these residual sodium cations will gradually be replaced by ammonium ions in the sodalite cages at sites I' or I. For cesium-exchanged sample 5, which contains ammonium ions mainly located in the sodalite cages, the line at δ = 6.5 is absent. The cesium ions (35 per unit cell) are located at sites II and III, thus preventing the nearby cation sites (especially sites II') from being occupied by ammonium ions. So we prefer to attribute the line at δ = 6.5 to ammonium ions at site II'. These findings are different from those obtained by Ozin and co-workers. They proposed that ammonium ions in the sodalite cages are located at site I' only.

When the residual sodium content is lower, the bulk NH₃/Na⁺ ratio will be smaller at a certain loading with ammonia. At a bulk NH₃/Na⁺ ratio between 0 and approximately 1, at least five types of ammonium species may exist for samples 3 and 4. We assign the signal at δ = 6.9 to ammonium ions located in a supercage, since this signal is also observed for sample 1 where the ammonium ions are located in the supercages only. The signals at δ = 6.5 and 8.1 are assigned to ammonium ions located in the sodalite cages at cation sites II' and I', respectively. The line near δ = 6.9 was already observed for different zeolites, but with a slightly different assignment. The line at δ = 8.1 is now reported for the first time.

Proton-Exchange of Ammonium Ions. Compared to the line at δ = 8.1, the lines at δ = 6.5 and 6.9 are shifted to higher field due to local proton exchange between an ammonia molecule and an acidic site. Clear indications for the existence of fast proton exchange comes from the experiments with excess loadings, which will be discussed further on (see the positions and areas of the "moving lines"). We note that for pyridine adsorption on acidic Y zeolites the lifetime of the pyridinium ions is 5 × 10⁻⁷ s at 313 K, which also implies fast exchange for this system. Translational jumps of pyridinium ions occur after an average time of 10⁻⁵ s, which is also fast compared to the NMR experiment. The signals observed in the region between δ = 6.9 or 6.5 and δ = 8.1 may then be assigned to fast exchange of ammonium ions between different cation positions. Since signals
due to ammonium ions and to the acidic protons are both observed in
one spectrum, the process of exchange apparently does not involve
the adsorption and desorption of ammonia at all acidic sites. This
can be rationalized in the following way. While in part of the cages ammonia interacts with Brønsted sites under
formation of ammonium species, Brønsted sites in other cages
may be completely unaffected because diffusion of ammonia
between these cages is slow. The local exchange process may
involve translational motion of ammonium ions between sites I'
and II' in the sodalite cages, but the occurrence of fast local
proton exchange cannot be excluded with the present experiments.
The residence time between two succeeding jumps is less than the
typical time scale of the NMR experiment (less than approximately
1 ms). At high loadings, when all acidic sites are saturated,
static signal at 5.5 and weak signal near 8.1 are observed for
both samples 3 and 4, indicating that some of the ammonium
ions in the sodalite cages do not participate in translational jumps.
The translational jumps can only occur at low loadings, when
only a few of the available cation positions in the cages are
occupied.

Since at low loadings the main contribution to the ammonium
species comes from the line at $\delta = 6.9$, we conclude that the
produced ammonium ions are predominantly located in the supernaces. So, removal of the sodalite cage protons ($\delta = 4.6$) does not
automatically result in sodalite cage ammonium ions. The protons
at O$_2$ can react easily with ammonia and produce ammonium
ions located in the supercages, e.g., at nearby cation sites II.
When ammonia reacts with protons at sites O$_2$, the nearest
cation sites for charge compensation may be sites of type III.
Only in the presence of cesium ions, almost all of the ammonium
ions are forced into the sodalite cages at site I' ($\delta = 8.1$). At high
loadings with ammonia on the other proeutzeolites, we observe
that some ammonium ions can be forced into the sodalite cages
at site II', without exchanging with other ammonium ions at site I'
or ammonia molecules in the supercages.

Freude and co-workers$^{20,21}$ reported that at high loadings fast
exchange occurs predominantly between ammonium ions and
ammonia molecules. This now determines the main features in
the MAS NMR spectra (Figures 6–8). Two species can be
discriminated. We observe a narrow signal, independent of the
loading at $\delta = 5.3$ (samples 1–4) or $\delta = 5.9$ (sample 5). For
the two deauminated Y samples, this signal is observed at $\delta = 5.5$.
From the observed positions we conclude that these signals are
due to a complex, formed by two ammonium ions ($\delta = 8.1$) in
fast exchange with one ammonium molecule ($\delta = 0.8$), which
is located in the sodalite cage (resulting in the signal observed at
$\delta = 5.9$). When such a species is located in the supercage,
additionally fast exchange with acidic protons occurs and the line
is shifted to $\delta = 5.3$. Since dealumination influences the position
for this line, and since the position for this line also seems to
correlate with the position of the lines for the acidic protons,
whereas for the dealuminated sample the position of the
ammonium line after partial reammoniation is observed at $\delta = 6.8$ (Table I), this also indicates that the exchange process involves
the interaction of acidic protons with ammonia.

The second species mentioned above undergoes fast exchange
with ammonia molecules and is the main signal in the NMR
spectra at high loadings with ammonia. Proton transfer from
ammonium ions to ammonia is the fastest step, and the chemical
shift of this species is determined by the chemical shift of a non-
exchangeable ammonium ion, that of an ammonia molecule, and
also by the total number of protons of the ammonium ions and
the ammonia molecules. We will refer to this signal as the moving
line. Ammonia in Na$^{+}$–Y gives rise to a signal at $\delta = 0.8$,
independent of the amount adsorbed. The line width, as measured
at room temperature at 300 MHz with a MAS frequency of 9
kHz, is 300 Hz at a loading of 5 ammonia molecules/unit cell
and increases to 470 Hz at 26 ammonia molecules/unit cell (see

<p>| TABLE II: Chemical Shifts of the &quot;Moving Line&quot; for the Different Samples at Different Loadings with Ammonia* |
|-----------------|-----------------|-----------------|-----------------|</p>
<table>
<thead>
<tr>
<th>sample</th>
<th>NH$_3$/unit cell</th>
<th>NH$_3$/NH$_4^+$</th>
<th>$\delta$ (ppm)</th>
<th>line width (Hz)</th>
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<tbody>
<tr>
<td>1</td>
<td>3</td>
<td>2.8</td>
<td>2.8</td>
<td>3.3</td>
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<td>3.9</td>
</tr>
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<td>1.4</td>
<td>4.3</td>
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<tr>
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<td>1.0</td>
<td>1.5</td>
<td>4.2</td>
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<tr>
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<td>32</td>
<td>0.7</td>
<td>1.5</td>
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<tr>
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<tr>
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<td>5</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* Positions in ppm and obtained from measurements at a field
strength of 7.0 T and a MAS frequency of 9 kHz. * Number of ammonia
molecules adsorbed. * Bulk and effective (only exchanging ammonium
ions are taken into account) ratios obtained after adsorption. * Calculated
chemical shift using $\delta = \{1/(4\text{NH}_3 + 3\text{NH}_4^+)\}(4\text{NH}_3 + \text{NH}_4^+ + 3\text{NH}_3\text{NH}_4^+)$
with $n$ representing the number of ammonium ions or ammonia molecules,
$\text{NH}_3\text{NH}_4^+ = 8.1 (6.9)$ and $\text{NH}_4^+ = 0.8$. * Strong overlap with intense line at $\delta = 5.2$. * No NH$_4^+$ present.

Table II). For the low loading, increasing the temperature from 295 K to 320 K results in an increase of the line width, whereas
at the high loading the line width is reduced. This is probably
due to different steric hindrances and exchange rates of the ammonia
molecules at different loadings and temperatures. This results
in differences in chemical shift (anisotropy), dipolar interactions,
and mobilities. However, the limited temperature range used
does not enable a more precise distinction.

When increasing the loading with ammonia for the acidic
zeolite to approximately 100 molecules/unit cell, we observe
a shift of a NMR signal to higher field (Figures 6–8). The position
of the signal is partially determined by the ratio NH$_3$/NH$_4^+$
in the sample. For the same sample this line shifts to higher field,
when the loading with ammonia is increased. However, the zeolite
composition plays also an important role. Samples with similar
bulk NH$_3$/NH$_4^+$ ratios show different chemical shifts for the
moving line and vice versa (Table II). In the preceding part we
already concluded that not all ammonium ions take part in the
exchange process with the ammonia molecules present. Probably
the local NH$_3$/NH$_4^+$ ratio determines the position of the moving
line. When we calculate such an effective NH$_3$/NH$_4^+$ ratio,
taking into account the number of ammonium ions, which do not
exchange with almost all ammonium molecules ($\delta = 8.1$, 6.5,
and also 5.3–5.9), we find a good agreement between the observed
and the calculated chemical shifts for the samples 1–4, when
using $\delta = 8.1$ for the chemical shift of a non–exchangeable
ammonium ion (see Table II). However, sample 5 shows a larger
shift than expected from the calculations. This indicates that
now exchange occurs via a more complicated process, which may
involve the acidic sites.

From the above we can conclude that the chemical shift of
non-exchanging or very slowly exchanging ammonium ions in
zeolite Y is $\delta = 8.1$ in both types of cages. Since also ammonium
ions are observed at higher field, we conclude that these species
are exchanging with acidic sites. However, since both Brønsted
sites and ammonium ions are observed in the same NMR
spectrum, this exchange process does not involve all acidic sites.
Probably, proton transfer is only from one ammonium ion to the
nearest oxygen atoms and back. This local exchange, which
involves only one or a few of the available acidic sites, is different
from the mechanism used by Michel and co-workers,$^{28}$ where all
adsorbed ammonia molecules are in equilibrium with all acidic
sites. However, the latter mechanism seems to be valid for the
moving line in the case of adsorption of excess ammonia.

Differences in chemical shifts for the ammonium species ($\delta = 6.9$
and 6.5) may be due to structural differences (e.g., local
concentration of oxygen atoms or Bronsted sites) which affect the exchange process. The resulting chemical shift of the protons is determined by the lifetimes of the ammonium ion and its dissociated form (the ammonia molecule and the Bronsted site) and also by the chemical shifts of these species participating in the local equilibrium. The ammonium species at δ = 6.9 are related to the hydroxyls at δ = 3.9, while the ammonium species at δ = 6.5 are related to the hydroxyls at δ = 4.6. This implies a longer lifetime for the ammonium ions at δ = 6.9 due to a stronger acid strength of the Bronsted sites involved. Further, this implies that the line at δ = 8.1 corresponds with non-exchanging or very slowly exchanging ammonium ions, in equilibrium with the most acidic protons. These ammonium ions are only observed in a large amount for cesium-exchanged sample 5 and in a considerably lower amount for highly exchanged samples 3 and 4. This result is in agreement with calorimetric measurements, where for completely exchanged Y zeolites a higher heat of adsorption for ammonia was observed than for Y zeolites with a degree of exchange of 85%.43

In the preceding part, differences in chemical shifts of the ammonium species were attributed to differences in proton exchange rates. Experiments over a more extended temperature interval are needed to confirm this suggestion. Differences in solvation by the zeolite walls at different cation sites may also influence the chemical shifts. Our results at high loadings with ammonia indicate, however, that the chemical shift of a very slowly exchanging or non-exchanging ammonium ion would be δ = 8.1 in both supercages and sodalite cages. Further, the dealuminated samples indicate that differences in proton exchange rates dominate: the line at δ = 5.3 is shifted to δ = 5.5, corresponding with a higher acidity for the dealuminated sample. This shift cannot be explained by solvation effects, since we observe at low loadings the ammonium line at a similar position (even at a slightly lower value for δ) than for the nondealuminated samples.

**Chemical Shift Dispersion, Dipolar Interactions.** The line width of the moving line is influenced by the zeolite composition, amount of ammonia adsorbed and the temperature (see Table II). Generally, an increase of the loading with ammonia causes a decrease of the line width. However, for the completely exchanged sample at the highest loading applied, the line width has increased again. The temperature dependencies for samples 1 and 3 are similar over the range studied. At the highest loadings an increase in line width is observed, after the temperature is increased from 295 to 320 K. At lower loadings the reverse is observed. For sample 4 we observe for all loadings an increase of the line width for a similar increase in temperature. Clearly, there are different factors present which affect the line width of the moving line in a different way (e.g., differences in mobility and/or chemical shift dispersion). A similar conclusion was obtained for sample 6 loaded with ammonia. Since increasing the spinning rate from 3 to 9 kHz results in a decrease in line width by only a factor of 1–1.5, we can conclude that the main contribution to the line width (at 9-kHz spinning rate) comes from the dispersion of the isotropic chemical shift, similar to the situation found for the bridging hydroxyls.22,23 There is, however, a measurable contribution from dipolar interactions at lower MAS speed.

The 1H MAS NMR signals of the Bronsted sites give rise to strong spinning sidebands (Figure 9 and Table III). The strongest spinning sidebands are observed for sample 5, which contains mainly sodalite cage protons. However, this sample has also a slightly higher aluminium content. But, from the data in Table III (samples 3, 4, and 7) it is clear that the different spinning sideband intensity does not arise from a different aluminium content in sample 5. The difference is caused by a stronger 1H–27Al dipolar interaction, due to a shorter H–Al distance for the protons located in the sodalite cages. Fenzke and co-workers25 found, from an analysis of the 1H MAS NMR sideband patterns, for the H–Al distance a value of 0.248 nm for protons in the superscages and a value of 0.237 nm for protons in the sodalite cages. This difference may be due to the interaction of the sodalite cage acidic protons with the two close oxygen neighbors. This interaction weakens the O–H bond, which leads to the occurrence of a LF-0H band in the infrared spectrum. Because of the bond order conservation principle,14 weakening of the O–H bond results in strengthening of the Si–O and Al–O bonds at the Bronsted site. So, this result is in shorter Si–O and Al–O bonds and a longer O–H bond. The overall result of these changes is a shorter H–Al distance for the Bronsted sites in the sodalite cages.

At increasing but still low loadings the relative intensities of the spinning sidebands for the Bronsted hydroxyls slightly increase. This is caused by the fact that the relative contribution of the sodalite cage protons to the peak height also increases.

When increasing the proton content of the zeolites (samples 1–3 in Table III), the relative intensities of the spinning sidebands for the Bronsted hydroxyls slightly increase. This is caused by the fact that the relative contribution of the sodalite cage protons to the peak height also increases.

Supplementary Table III: Mean Sideband Intensities of the First Spinning Sidebands as Percentages of the Main Signals for MAS Frequencies of 3 and 6 kHz

<table>
<thead>
<tr>
<th>sample</th>
<th>loading of NH3/unit cell</th>
<th>relative sideband intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si–OH–Al</td>
<td>NH4+</td>
</tr>
<tr>
<td></td>
<td>δ</td>
<td>kHz</td>
</tr>
<tr>
<td>1</td>
<td>0.0</td>
<td>3.9</td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>3.9</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>3.9</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>3.9</td>
</tr>
<tr>
<td>5</td>
<td>0.0</td>
<td>4.6</td>
</tr>
<tr>
<td>6</td>
<td>0.0</td>
<td>4.6</td>
</tr>
<tr>
<td>7</td>
<td>0.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>

At increasing but still low loadings the relative intensities of the spinning sidebands for the Bronsted hydroxyls and for the ammonium ions (Figures 9 and 10) both remain constant, which is in agreement with our previous conclusion that the adsorbing ammonia molecules show no preferences for specific acidic sites in a particular cation. The spinning side bands of the ammonium ions (four protons) are of different origin than those for the Bronsted sites (one proton) and therefore not as strong (see Table III).27 In the case of low loading (not all acid sites have reacted) we observe the weakest spinning sidebands for the samples with the highest sodium content (samples 1 and 2). For sample 5, with the ammonium ions located at site I, the strongest sidebands are observed. From Table III we see, that only a part of this increase in intensity may be attributed to differences in the Si/Al ratio or exchange degree. So we may conclude that these ammonium ions are more rigidly bonded. When excess ammonia is added, the sidebands decrease in intensity for all samples, presumably due to fast exchange between ammonium moieties with the mobile ammonia molecules. The spinning sidebands for the moving line are only very weak (a few percent or less at a spinning frequency of 3 kHz). The spinning sidebands of δ = 6.5 and 5.3–5.9 are somewhat stronger (approximately 5–10% at 3 kHz). This order of sideband intensities is in agreement with the differences in fast exchange found for the different signals, resulting in the strongest spinning sidebands for the species with the highest ammonium character.

At low loadings the line widths of the NMR signals of the ammonium ions are sensitive to the MAS frequency (see Table IV). The changes in the line widths with increasing MAS frequency are determined by the composition of the sample (e.g., Na+, H+, NH4+) and the strength of the magnetic field. In a weaker field the influence of spinning is more pronounced. These
results indicate not only that chemical shift dispersion determines the line width but also that dipolar interactions are of importance. As for the Brønsted sites, differences in line widths for the ammonium signals may be due to different dipolar interactions and to differences in chemical shift dispersion. Since increasing the spinning rate from 3 to 9 kHz results in a reduction of the line width by only a factor 1–2, the main contribution to the line width is the isotropic chemical shift dispersion. At 320 K, the effect of the MAS frequency is somewhat larger at very low loadings. Due to the temperature increase, the mobility of the ammonium ions has increased and the dipolar interactions are decreased.

At high loadings, the observed bands are narrower (see the moving line in Table II) and less sensitive to the MAS frequency. This is due to the fast exchange between ammonium ions and highly mobile ammonia molecules (see above).

The influence of the temperature on the line width is probably rather complex. At a MAS frequency of 9 kHz increasing the temperature results in a reduced line width for all samples. However, since the effect of the MAS frequency depends also on temperature, we observe at 3 kHz and at very low loadings an increase of the line widths for ammonium ions in supercages (samples 1 and 2), while the line width for ammonium ions at site 1' in the sodalite cages (sample 5) decreases slightly (8%) with increasing temperature. So the ammonium ions in the sodalite cages at site 1' are more sensitive to temperature changes than the ions at other locations. Increasing the temperature probably results in an increased population of sites with higher mobility and hence results in an increase of the chemical shift dispersion. However, at the same time the dipolar interactions may be reduced. From our results, we may conclude that both effects are indeed operative. However, from the rather small influence of the spinning rate on the line widths, we conclude that the main contribution comes again from the isotropic chemical shift dispersion.

**Comparison with Earlier 15N NMR Experiments.**

The results from our 1H MAS NMR experiments can be compared with the result of 15N CP MAS NMR experiments by Earl and co-workers. When only a small amount of ammonia is adsorbed on the proton form of the Y zeolite, they observed a line at δ = -357 due to ammonium ions bonded to the lattice. This signal is probably related to the line we observe at δ = 6.9. When excess ammonia is adsorbed, lines near δ = -353, -358, -361, and -364 are observed. The line at δ = -353 is attributed to ammonium ions coordinated to the lattice. This line may be correlated with the weak line we observe near δ = 8.1. The other three features in the work of Earl were assigned to ammonium ions, which are hydrogen bonded to ammonia. We only observe two lines (δ = 5.3 and the moving line) for the species involving hydrogen bonding with ammonia. Since we observe for a comparable zeolite sample also a line at δ = 5.2, one of the weak lines at δ = -358 or -361 may correspond to this line in our spectrum, assigned to exchanging ammonium ions.

**Table IV: Line Widths of the Ammonium Signals (δ = 6.9 and 8.1) Observed at Different Loadings on Different Zeolite Samples for Different MAS Frequencies**

<table>
<thead>
<tr>
<th>sample</th>
<th>loading of NH3/unit cell (ppm)</th>
<th>line width (Hz) at 9.4 T</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>δ = 6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3 kHz</td>
</tr>
<tr>
<td>1</td>
<td>3.6</td>
<td>263</td>
</tr>
<tr>
<td>2</td>
<td>3.6</td>
<td>410</td>
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<tr>
<td>3</td>
<td>10.2</td>
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<td>4.5</td>
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<td>7</td>
<td>3.0</td>
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</table>

**Conclusions**

Room temperature adsorption of ammonia on zeolite Y shows that protons in supercages and sodalite cages react with this small strong base, without any preference for specific sites. Differences in acidity for Brønsted sites cannot be probed directly by room temperature adsorption of ammonia, since here the most important factor is the protonation of ammonia.

Adsorption of ammonia results in the formation of at least five NMR signals, depending on zeolite composition and loading with ammonia. Ammonium ions in the large supercages are observed at δ = 6.9 and ammonium ions in the small sodalite cages are observed at δ = 6.5 (site 1' and δ = 8.1 (site 1'). At low loadings, proton exchange between the ammonium ions with acidic sites in other cavities is slow on the time scale of the NMR experiment. But, proton transfer from an acidic site to a nearby ammonia molecule and back can be fast. In such a case, a signal is observed with a chemical shift smaller than δ = 8.1, the value for a non-exchanging ammonium ion. Additionally to this fast exchange, fast translational jumps of ammonium ions to nearby cation sites may occur at low loadings, e.g., jumps between the sites 1' where local proton exchange is slow to sites 11' where local proton exchange is fast.

When an excess of ammonia is adsorbed onto the zeolite, a concentration dependent signal is found, indicating that proton exchange between ammonium ions and ammonia molecules is fast and proton exchange with Brønsted sites plays a negligible role. The position in the NMR spectrum of this line depends on the effective NH₃/NH₄⁺ ratio (δ = 7 at low loadings and approaches δ = 1 at high loadings). At the same time, however, signals due to ammonium ions are still observed. So not all ammonium ions take part in the exchange processes. Further, clusters involving mainly fast exchange of two ammonium ions with one ammonia molecule can be observed at δ = 5.2–5.9. A small contribution to this signal comes from fast exchange involving these clusters and acidic hydroxyls.

After adsorption of small amounts of ammonia onto the acidic zeolite, the major part of the ammonium ions are located in the larger supercages. At high loadings with ammonia, and especially when large cesium ions are present in the supercages, the ammonium ions are forced into the smaller sodalite cages. For all species, except for the ammonium ions observed at δ = 8.1, proton exchange is fast on the time scale of the NMR experiment.

Finally, it has to be noted that the different ammonium species give rise to spinning sidebands of different intensities. The same holds for the different types of Brønsted sites, which give rise to even more intense spinning sidebands. So, for accurate quantitative studies of zeolite acidity by ammonia adsorption high MAS frequencies (9 kHz or more) should be used, at least at field strengths of 9.4 T or larger.

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References and Notes

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