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A Multinuclear Solid-State NMR Investigation of the Chemisorption of Ammonia on γ-Alumina

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Abstract: The surface preparation-dependent interactions of ammonia with γ-alumina were explored via solid-state ^{15}N and ^{2}H NMR spectroscopies. ^{15}N experiments demonstrated an unresolved distribution of ammonia surface species. Wide-line ^{2}H line shapes and T_1 experiments indicate the presence of three motionally distinct deuteron resonances associated with the ammonia adsorbate. An ammonia resonance indicative of rapid motion about the threefold symmetry axis was isolated for the more sparsely hydrated surfaces and has been identified as the Lewis complex resonance. T_1 experiments show for this site that motion about the threefold axis is diffusive. A second deuterium resonance has been identified as a surface hydroxyl species by comparison with D_2O on γ-alumina experiments. This resonance shows a direct proportion of intensity with surface hydroxyl concentration, demonstrating the exchange of Brønsted hydrogens with ammonia hydrogen atoms. A third component of the deuterium line shapes has been associated with surface Brønsted ammonium species and appears to be comprised of a distribution of motionally averaged species. The experimental line shapes were simulated, and the relative Lewis and Brønsted site populations of ammonia were estimated.

The properties of solid catalysts have been the subject of study for several years,[1] especially in the petroleum industry where these catalysts are used for the processing of hydrocarbons on a large scale. These reactions include cracking,[2] skeletal isomerization,[3] and polymerization.[4] Surface acidity is a key factor of catalytic activity and much attention has been directed toward the characterization of surface acid binding sites as to their type, quantity, and physical environment.[5,6] Some of the techniques which have been developed and employed are pH indicator methods in solution,[7] gravimetric determination of the adsorption of gaseous bases,[8] and characterization of surface-adsorbed gaseous bases by infrared spectroscopy.[9] In recent years several reports have appeared involving the application of modern solid-state NMR methods to the area of surface chemistry.[10] These applications have involved ^{1}H,[11] ^{2}H,[12] ^{13}C,[13] ^{15}N,[14] and ^{31}P[15] NMR studies of a variety of materials adsorbed to surfaces.

In the present investigation we have employed ^{2}H and ^{15}N NMR spectroscopies to study the chemisorption of ammonia on a γ-alumina surface. This system has been studied by previous authors such as Clark et al.[8b] who have determined the isosteric heats of adsorption. Those experiments demonstrated that ammonia is bound relatively tightly to γ-alumina at low surface coverages. Infrared spectroscopic studies[9] have yielded valuable information concerning the types and amounts of ammonia species which are present on alumina and modified alumina surfaces.

The present study utilizes wide-line ^{2}H NMR to investigate the details of molecular motion in the solid state. It is well-known that the ^{2}H line shape is sensitive to motional processes occurring on the order of microseconds.[18] With these methods we have found that ammonia can exchange hydrogens with the surface, and we have been able to separate the contributions to the ^{2}H line

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shape arising from Brønsted and Lewis sites on the surface. We shall demonstrate that this separation of Brønsted and Lewis sites cannot be accomplished with either ^{15}N or ^{31}P NMR for γ-alumina surfaces. ^{2}H NMR techniques represent a novel way to characterize the nature of Brønsted and Lewis acid sites on a surface both with respect to their motion and their relative populations.

Experimental Section

Samples. The γ-alumina samples were prepared from carefully ground high-purity pellets (Norton catalyst support No. SA6173; 220 m^2/g). Samples (1.0 g) were added to glass break-seal tubes (Pyrex or quartz), dried under vacuum, and flame sealed under vacuum. Measured samples of purified $^{15}NH_3$ or ND_3 (Merck Sharp and Dohme gases dried over freshly cut sodium metal and vacuum distilled) were placed in the other chamber of the break-seal tube (370 μmol corresponds to approximately 25% of a monolayer where one monolayer is defined in this study as 4 molecules per 100 Å^2) and flame sealed under vacuum. The adsorbent and adsorbate were united and equilibrated by shattering the seal and heating the tube at 120 °C for 1–3 h before slowly cooling to room temperature. Surface samples of $P(CH_3)_3$ and D_2O were prepared in an analogous manner.

Just prior to performing the NMR experiments the break-seal tubes were opened under dry nitrogen, and the sample was packed into a precision machined ceramic rotor fitted with Kel-F end caps. This sample handling was performed inside of a Vacuum Atmospheres drybox.

Each of the samples was initially dried by evacuation at 25 °C for 8 h, followed by the gradual elevation of the temperature to 150 °C (4 h; approximately 30 °C/h). This initial procedure resulted in the removal of the majority of the hydroxyl groups from the sample without sintering the alumina. Three individual methods for vacuum drying the γ-alumina samples were employed. Partially dehydroxylated alumina (PDA) samples were prepared by evacuating the sample for 8 h at 350 °C to a final pressure of 10^{-5} torr. Intermediately dehydroxylated alumina (IDA) samples were prepared by evacuating the starting material at 510–550 °C, calcining the sample under O_2 for 30 min (three 10-min intervals with intermittent evacuation), and evacuating for 3 h at 610 °C. Extensively dehydroxylated alumina (EDA) samples were obtained by calcining the starting material under O_2 for 1 h at 815 °C and evacuating for 5 h at the same temperature to an ultimate pressure of 10^{-6} torr.

NMR Measurements. ^{15}N and ^{2}H solid-state NMR spectra were acquired with a Bruker WH-400 spectrometer at resonance frequencies of 40.55 and 61.42 MHz, respectively. ^{15}N NMR spectra for each surface containing 25% of a monolayer $^{15}NH_3$ were obtained under a variety of conditions; magic angle spinning[19] and static powder resonances were each observed via cross-polarization[20] and with Bloch decays with gated proton decoupling.

In an attempt to gain a better understanding of the distribution of Lewis and Brønsted acid sites on γ-alumina, we also obtained solid-state ^{31}P spectra of $P(CH_3)_3$ chemisorbed on these surfaces. The results of these experiments are analogous to those already reported.[15b] The ^{31}P spectra were obtained on a Varian XL-300 equipped with a broad-band tunable Doty Scientific MAS probe. The resonance frequency for ^{31}P on this spectrometer is 121.4 MHz.

The solid-state deuterium NMR spectra were obtained utilizing a home-built wide-band receiver[21] capable of a 5-MHz simultaneous quadrature digitization rate. The probe employed in a single resonance horizontal coil 5-mm NMR powder probe purchased from Doty Scientific Inc., whose impedance was carefully matched to a high-power duplexer. Careful attention was given to impedance matching, bandwidth, and gain in all subsequent stages of amplification and filtering.

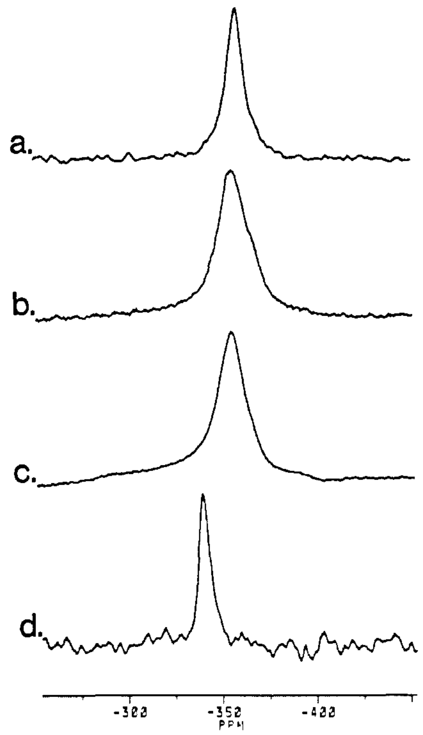

Figure 1. 40.55-MHz ^{15}N MAS spectra of ^{15}N-enriched ammonia on γ-alumina (25% monolayer; 1 molecule/100 Å^2): (a) PDA surface obtained with Bloch decays, 816 15-s repetitions; (b) IDA surface obtained with cross-polarization, 6432 0.5-s repetitions, 2-ms contact time; (c) EDA surface obtained with cross-polarization, 9600 0.5-s repetitions, 2-ms contact time; (d) non-^{15}N-labeled NH_3:$AlCl_3$ complex ^{15}N MAS spectrum obtained with cross-polarization, 12 660 2-s repetitions, 2-ms contact time. Chemical shifts are relative to 0.1 M NH_4NO_3.

Deuterium spectra were obtained using a quadrupole spin-echo[22] pulse sequence. Ninety degree pulse widths of 1.9 μs were attained with 900-W pulse power at 61.424 MHz. The pulse sequence timing parameters and receiver phase were optimized by observing the line shapes for hexamethylbenzene-d_{18} and perdeuterated polyethylene. Subsequently, only nominal zero-order spectral phasing was necessary to adjust the phase of the powder patterns. We define the separation between the perpendicular edges (the "horns") as $\omega_Q/2\pi$. This separation is three-fourths of the motionally averaged quadrupole coupling constant.

Quadrupolar spin echo spectra were obtained for each of the ND_3/alumina samples. An ambient-temperature study of the dependence of the line shapes on the parameter τ was performed in the range of 10–200 μs. No line-shape distortion was observed, indicating that molecular motion is either very slow or in the limit of fast exchange. An inversion recovery quadrupole echo T_1 experiment was performed on each ND_3 sample to resolve line-shape components and to characterize molecular motion.

In order to investigate the consequences of exchange of deuterons between NH_3 and the alumina surface, we obtained ^{2}H spectra for samples of alumina exposed to D_2O. We examined the ^{2}H NMR of a PDA surface within 8 h of its preparation and after storage of the same sample for 30 days at −10 °C.

Results and Discussion

Solid-state ^{15}N NMR experiments were performed to determine chemical states of the surface-associated ammonia and thus the chemical environment of the adsorption sites. The ^{15}N spectra of Figure 1 depict a surface-preparation-dependent distribution of resonances which cover a chemical shift range of approximately 30 ppm.

The spectrum of NH_3 on PDA (Figure 1a) displays a resonance distribution centered at −362 ppm (relative to 0.1 M NH_4NO_3), similar to inorganic ammonium ions (−352 ppm).[23] The observed

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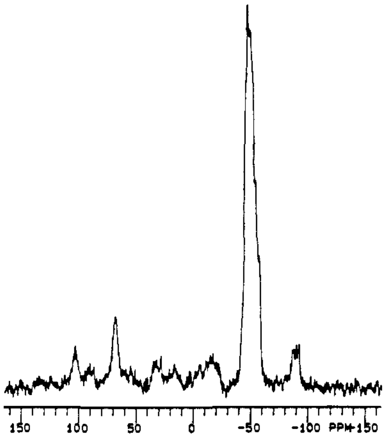

Figure 2. 121.4-MHz ^{31}P CP/MAS spectrum of trimethylphosphine adsorbed to γ-alumina (PDA; 25% monolayer).

line width at half-height is 9 ppm. This same resonance distribution was observed both in the presence and the absence of magic angle spinning (MAS). The ^{15}N MAS spectra of NH_3 on IDA (Figure 1b) and EDA (Figure 1c) surface samples exhibit broader, less symmetric, and slightly more deshielded resonances, their resonance distributions shifting toward the resonance of the model Lewis complex $NH_3{:}AlCl_3$ (Figure 1d). The spectrum of NH_3 on EDA exhibits a line width of 15 ppm and a line-shape maximum at −358 ppm. The spectrum of NH_3 on IDA exhibits a shielding maximum at −360 ppm and a line width of 28 ppm. The Lewis acid–base complex ($NH_3{:}AlCl_3$) spectrum has a line width of 5 ppm and a isotropic shielding value of −342 ppm.

The results of the ^{15}N experiments suggest a model of a surface containing a distribution of Brønsted and Lewis acid adsorption sites. As the temperature for surface evacuation is raised, more hydroxyl protons are desorbed (as H_2O), removing Brønsted sites and uncovering more Lewis acid sites. These experiments demonstrate the utility of ^{15}N-labeled ammonia as a probe of surfaces containing diverse acid sites. However, the results of these experiments are disappointing, as the ^{15}N chemical shifts are not sufficient to afford absolute resolution of the various species present. Hence it would be very difficult to quantify the number of Brønsted vs. Lewis sites on this surface utilizing ^{15}N NMR.

It is interesting to contrast our ^{15}N experiments with the ^{31}P experiments recently reported by Lunsford, Rothwell, and Shen.[15b] In their work they utilized $P(CH_3)_3$ (a relatively weak base compared to NH_3) to probe the various acid sites on zeolites and a γ-alumina surface. In the case of γ-alumina, they only observed ^{31}P resonances associated with the Lewis acid species. We repeated their experiments on our surface preparations with both Bloch decays and cross-polarization methods and essentially observed the same results (Figure 2). This representative spectrum is composed of resonances at −50 and +67 ppm (both of which are flanked with first-order spinning sidebands) which the authors[15b] have identified as arising from a Lewis acid species and some oxidation products, respectively. The ^{31}P NMR results have the advantage of a larger chemical shift range, so that one can obtain absolute resolution of the various species present. However, because of the lower basicity of $P(CH_3)_3$ and phosphines in general, misleading information about the relative numbers of Brønsted and Lewis sites on the surface may result from the ^{31}P NMR method. For example, the ^{15}N spectra clearly show a distribution of Brønsted and Lewis acid sites and that this distribution is sensitive to the sample preparation, whereas the ^{31}P experiments on the same surfaces (data not shown) are insensitive to the presence of the Brønsted sites. Hence, one can only conclude from the ^{31}P NMR results that the Brønsted acids on γ-alumina are too weak to protonate trimethylphosphine.

Solid-state ^2H NMR experiments offer the opportunity of characterizing the motional freedom of ammonia species at a surface and the characteristics of its binding sites. By utilizing ^2H line-shape analysis and T_1 experiments, and by comparing ^2H spectra of water and ammonia bound to a γ-alumina surface, the ^2H spectra can be interpreted in terms of distributions of ammonia species. A few simple motional models serve to explain many of the features of the spectra. The ^2H spectra obtained for ND_3 adsorbed on the various dehydroxylated γ-aluminas (Figures 3–5) indicate the presence of a deuterated surface and a variety of surface-associated ammonia species which are identified as Lewis acid adducts and one or more Brønsted acid species.

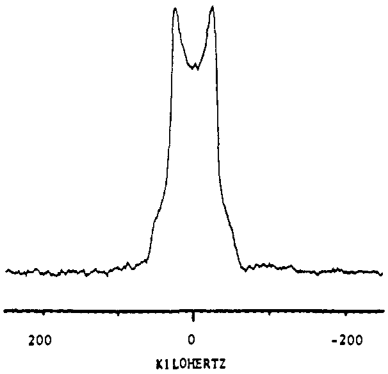

Figure 3. 61.4-MHz ^2H quadrupolar spin echo spectrum of perdeuterated ammonia on γ-alumina (EDA): 3800 0.5-s repetitions, 40-μs echo delay, 25% monolayer coverage.

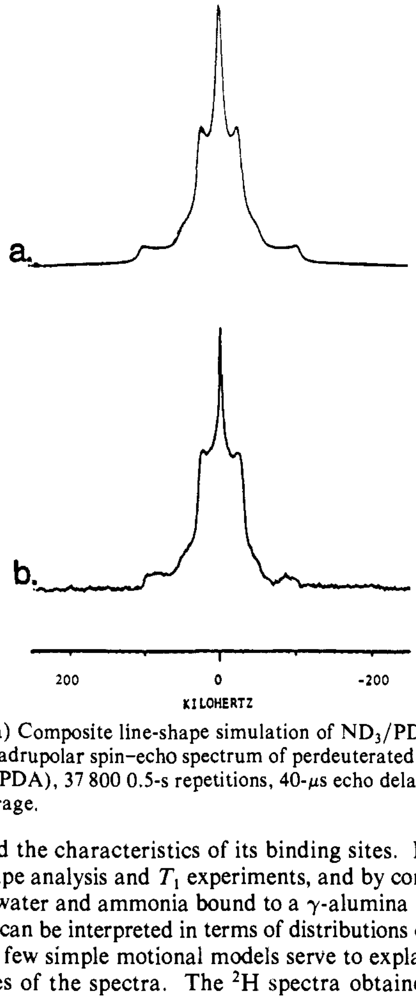

Figure 4. (a) Composite line-shape simulation of ND_3/PDA; (b) 61.4-MHz ^2H quadrupolar spin-echo spectrum of perdeuterated ammonia on γ-alumina (PDA), 37 800 0.5-s repetitions, 40-μs echo delay, 25% monolayer coverage.

The ^2H spectrum for the sample of ND_3 on EDA (Figure 3) shows an isolated resonance with $\omega_Q/2\pi$ of 54 kHz and $\eta = 0$. This resonance is present in all of the spectra and is observed to increase in intensity with the surface drying temperature. This value of $\omega_Q/2\pi$ agrees with all previously observed values for ammonium residues[24] and corresponds with the rapid reorientation of the residue about its threefold axis.

The ^2H line-shape spectrum (Figure 3) for ND_3 on EDA indicates motion about the threefold axis. However, the details of

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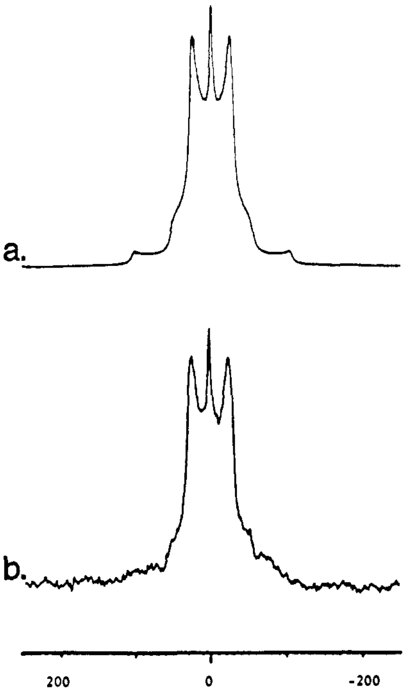

Figure 5. (a) Composite line-shape simulation of ND_3/IDA; (b) 61.4-MHz ^2H quadrupolar spin–echo spectrum of perdeuterated ammonia and γ-alumina (IDA), 3800 0.5-s repetitions, 40-μs echo delay, 25% monolayer coverage.

this motion are lost because a fast motion limit three site rotation jump process yields a line shape which is identical with that for rapid diffusion about that axis. This detailed motion may be recovered by determining the orientational dependence of the deuterium spin–lattice relaxation time T_1. Torchia and Szabo[25] have shown that the relaxation rate of a deuteron which is attached to a tetrahedral center and performing rapid diffusion about a threefold axis (other than the axis the deuteron is aligned with) is given by

$$1/T_1 = 8\omega_Q^2\tau/27 \qquad (1)$$

where τ is the reciprocal of the diffusion rate. The expression for the relaxation rate of a deuteron undergoing rapid threefold site jumps is given as

$$1/T_1 = (4\omega_Q^2/27\kappa)(1 + \cos^2\theta) \qquad (2)$$

where θ is the angle between the laboratory z axis (the magnetic field direction) and the jumping axis, and κ is the site exchange rate. The rate expression for the diffusion model does not depend upon the powder angle θ and hence the relaxation is isotropic. In contrast to this dependence the relaxation rate for the jump model is anisotropic. The parallel components, $\theta = 0°$, of the line shape would relax twice as quickly as the discontinuities at $\theta = 90°$. ^2H inversion recovery relaxation experiments for the ND_3/EDA sample (Figure 6) demonstrate the isotropic relaxation of the Lewis site species. This clearly demonstrates that the reorientational process for ND_3 at the Lewis site is diffusive.

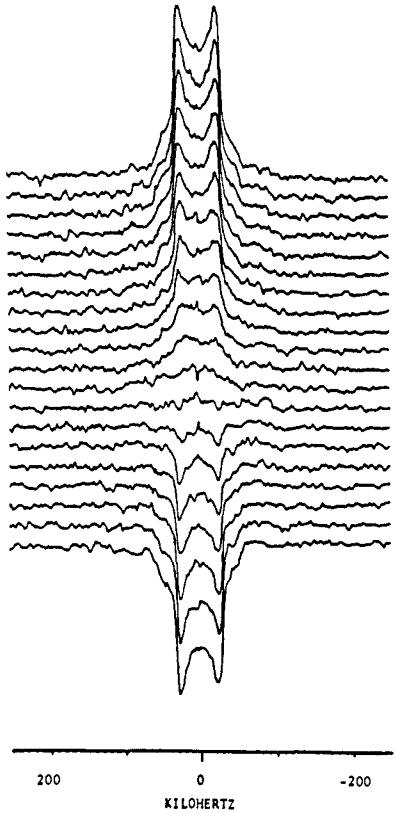

Figure 6. 61.4-MHz ^2H inversion recovery quadrupolar spin–echo spectra of ND_3/EDA: 1200 0.6-s repetitions per experiment, temp 19 °C, T_1 = 200 ms.

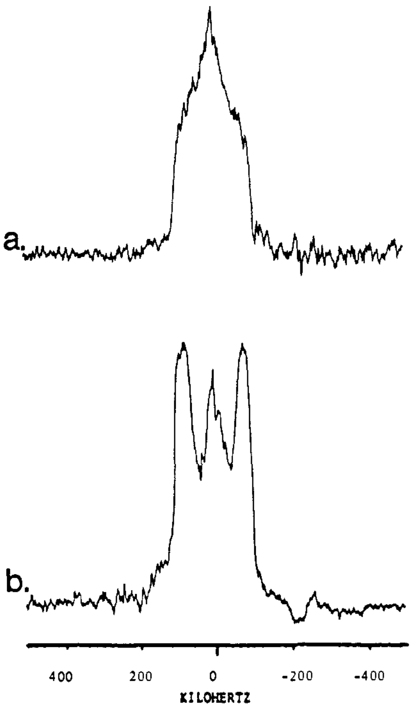

Figure 7. 61.4-MHz ^2H quadrupolar spin–echo spectrum of perdeuterated water on PDA γ-alumina, 25% monolayer coverage: (a) freshly prepared sample, 13 256 2-s repetitions; (b) reacted sample, 88 000 0.5-s repetitions.

The ^2H spectrum of ND_3 on PDA (Figure 4b) displays a broad resonance with $\omega_Q/2\pi$ = 210 kHz. This resonance is too broad to be an ammonium resonance.[26] However, the 210-kHz splitting does correspond with O–D deuterons.[27] A ^2H NMR experiment with a PDA surface containing D_2O (Figure 7a) (in equimolar surface concentration to the ND_3 samples) revealed an η = 1 line shape with $\omega_Q/2\pi$ = 210 kHz which is the same as the broader resonance in the ND_3/PDA ^2H spectrum. To generate hydroxyl resonances, the sample was allowed to undergo hydrogen exchange. The same sample was stored at −10 °C for 30 days and run at room temperature (Figure 7b) to reveal the ^2H resonance evolving

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(25) Torchia, D. A.; Szabo, A. *J. Magn. Reson.* **1982**, *49*, 107–121.

(26) The observed quadrupolar splitting for the ammonium residue is only approximately 54 kHz, and even if all reorientational motion were to cease the static $\omega_Q/2\pi$ is only approximately 160 kHz.

(27) The exchange of ammonia hydrogen atoms with γ-alumina hydroxyl groups has been observed previously[5c] via infrared spectrophotometry. Aluminas are also known to catalyze the conversion of o-H_2 to p-H_2, hydrogen gas isotopic exchange, methane isotopic scrambling, and the isotopic exchange of D_2 with a variety of unsaturated hydrocarbons.[6]

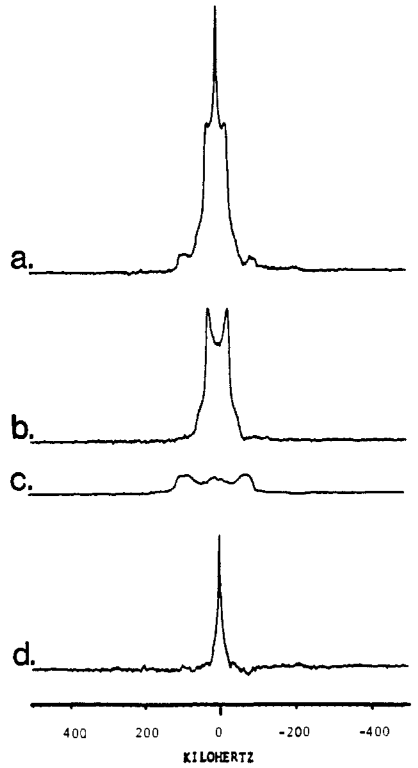

Figure 8. The subtraction of identified ^2H line-shape components from the spectrum of ND_3/PDA: (a) ND_3/PDA, (b) ND_3/EDA, (c) reacted D_2O/PDA, (d) optimized difference spectrum displaying the approximate line shape of the Brønsted ammonium species.

toward an $\eta = 0$ line shape with the same value of $\omega_Q/2\pi$. Computer simulations for the ND_3/PDA spectra (Figure 4a) show that the 210-kHz component contributes approximately 27% of the spectral area. This broad component shows a rapidly diminishing contribution to the spectra of ND_3 on IDA and EDA suggesting a direct correlation with surface hydroxyl concentration.[28] These results clearly demonstrate that NH_3 can exchange hydrogens with the surface hydroxyl groups on γ-alumina. However, these spectra do not point to a specific mechanism for this exchange process. The surface preparation dependence of both the 210- and the 54-kHz ($\eta = 0$) resonances supports the identification of the corresponding chemical species as deuteroxyl and Lewis-site-associated ammonia species, respectively. As the surface drying temperature is raised, Brønsted hydroxyl acid sites are removed as H_2O, and Lewis acid sites are generated by the desorbing water molecules. The absence of the deuteroxyl resonance in the ND_3/EDA spectrum (Figure 3) shows that the Lewis site ammonia species is not responsible for the observed hydrogen exchange.

Having identified two distinct ^2H resonances, we now consider the resonance (or resonances) contributing to the center of the ND_3/PDA line shape. Unlike the identifiable deuteroxyl resonance (Figure 7) and the distinct Lewis site resonance (which is isolated in Figure 3), the component at the center of the ND_3/PDA and ND_3/IDA spectra (Figures 4 and 5) is obscured by other resonances and must be isolated by a subtraction technique. By subtracting appropriately scaled spectra of the ND_3/EDA and hydrogen-exchanged D_2O/PDA samples from the spectrum of the ND_3/PDA sample, an approximate line shape is obtained (Figure 8d). This resonance is most intense at the center and broadens to a base-line width of 54 kHz. Subsequently this line shape shall be referred to as the "isotropic component" of the

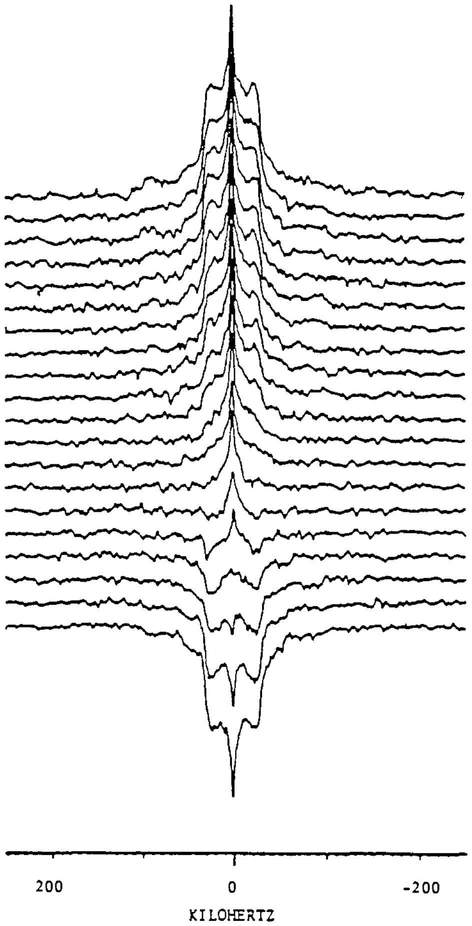

Figure 9. 614-MHz ^2H inversion recovery quadrupolar spin-echo spectra of ND_3/PDA: 1200 0.6-s repetitions per experiment, temp 19 °C.

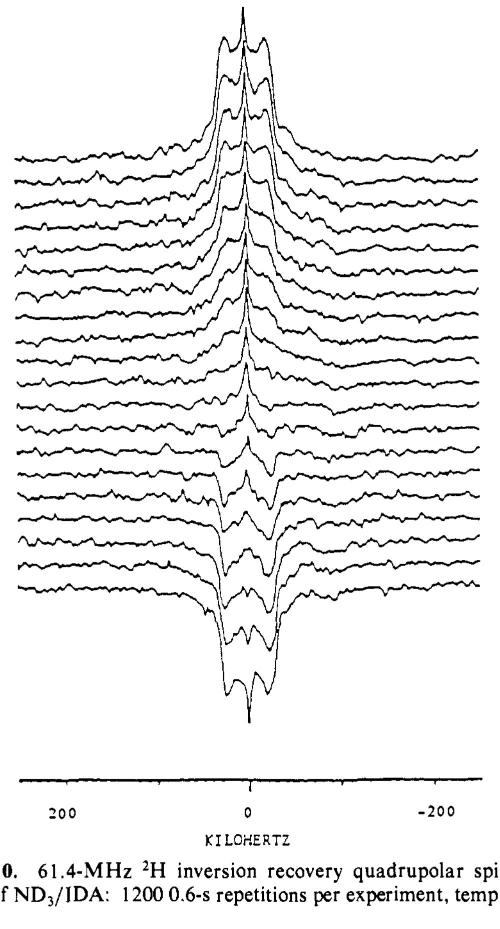

Figure 10. 61.4-MHz ^2H inversion recovery quadrupolar spin-echo spectra of ND_3/IDA: 1200 0.6-s repetitions per experiment, temp 19 °C.

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[28] Previous infrared spectroscopic studies of NH_3 on γ-alumina[9c] have revealed the formation of new hydroxyl groups via dissociation of ammonia to form an NH_2^- species, but this was estimated to account for an optimum of 1 in every 10 NH_3 molecules[9c] and accordingly would contribute only 3% to the spectral area (this optimum value pertains only to the surfaces with the least hydroxyl sites whereas we are now considering the surface with a high concentration of hydroxyl sites present).

surface spectra. To resolve the resonances contributing to the line shapes, a series of inversion recovery experiments were performed on the PDA and IDA surfaces containing ND_3 (Figures 9 and 10, respectively). For these experiments the center component of the line shape was observed to relax at a rate significantly faster than the other components. This resonance resembles the isotropic line shape obtained by the difference spectra (Figure 8d).

To account for this isotropic component, a highly mobile ammonium surface species must exist. This species must, however, meet the condition of nonisotropic reorientation. The rapid and truly isotropic reorientation of the ^2H quadrupolar tensors would result in the averaging of the quadrupolar interaction to zero (since the quadrupolar tensor is traceless), leaving only the Zeeman interaction. The quadrupolar echo experiment acts like a "quadrupolar filter" because the refocusing of magnetization relies upon the presence of a residual quadrupolar interaction, so any rapid isotropically reorienting species would be invisible to these experiments. The observed line shapes are insensitive to the variation of the quadrupolar echo delay (τ_{qe}) in the range of 10–200 μs.

To quantify the relative contributions of the individual resonances to the ND_3/PDA (Figure 4b) and the ND_3/IDA (Figure 5b) spectra, composite line-shape simulations (Figures 4a and 5a) were generated and compared with the experimental line shapes. The elements of these composite line shapes are simulated quadrupolar echoes (time domain data) for the Lewis, Brønsted (approximated with an isotropic resonance), and deuteroxyl species. The deuteroxyl resonance was approximated by the combination of an $\omega_Q/2\pi = 210$ kHz ($\eta = 0$) resonance and an $\omega_Q/2\pi = 210$ kHz ($\eta = 1$) resonance in the ratio of 2:1, respectively, and treated as a single echo for the simulations. The Lewis and deuteroxyl resonances were each given an initial Lorentzian line broadening of 4 kHz. For the simulation of ND_3 on PDA, the Brønsted resonance was given an initial line width of 1 kHz and combined in varying ratios with the Lewis and the deuteroxyl resonances before the application of additional exponential multiplication (9.4 kHz) and Fourier transformation. For the simulation of ND_3 on IDA, the Lewis and deuteroxyl resonances were combined and further Lorentzian line broadening (6.4 kHz) was applied. The Brønsted resonance (with a total line width of 4 kHz) was added and Fourier transformed with the other resonances. The optimization of fit to the experimental line shapes was facilitated with a simplex algorithm.[29]

The composite simulation of the ND_3/PDA spectrum (Figure 4) indicates the contribution of approximately 56, 27, and 17% for the Lewis, deuteroxyl, and Brønsted components, respectively. The simulations of the ND_3/IDA line shape (Figure 5) show that the relative contributions are 81, 15, and 4% for the same respective resonances. These percentages can be used directly to estimate the relative populations of ammonia-occupied sites, if we assume that the ammonia species of the Lewis site does not participate in hydrogen exchange (i.e., it finds its Lewis site before significant exchange occurs). For the composite line-shape simulations, the total line width for the Brønsted resonance was 10.4 kHz for the PDA sample, and 4.0 kHz for the IDA sample. The decrease in line width with higher surface preparation temperature indicates a decrease in the heterogeneity of motional averaging of the Brønsted species.

An error analysis was performed on each composite simulation by determining the sensitivity of the relative intensities of the most accurately measurable features of the line shapes (i.e., the center, the 54-kHz splittings, and the 210-kHz separations). The results indicate the line shape is two or three times more sensitive to the relative contribution of the Brønsted resonance compared with the Lewis resonance, and between 6 and 20 times more sensitive as compared with the deuteroxyl resonance. Therefore, population of the deuteroxyl sites will be prone to the most error.

Like the broad hydroxyl resonance, the isotropic component decreases with decreasing surface hydroxyl concentration (Figures 4, 5, and 3). As an interesting comparison, variable-temperature experiments performed on the ND_3/PDA sample in the temperature range from 295 to 80 K (Figure 11) indicate the same gradual decrease and finally the disappearance of the isotropic component at 80 K. The trend for diminishing intensity which is observed for the isotropic component in the variable-temperature experiments arises from the removal of thermal energy from the system. A simple motional model can explain this behavior.

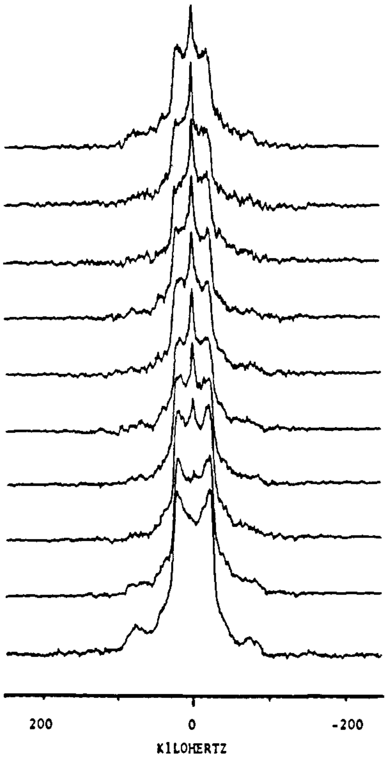

Figure 11. 61.4-MHz ^2H variable-temperature quadrupolar spin–echo spectra of ND_3/PDA: 4096 0.5-s repetitions per experiment, 40-μs echo delay. Experimental temperatures (in descending order) are 294, 275, 250, 225, 200, 175, 150, 125, 97, 80 K.

Envision a tetrahedral ND_4^+ molecule which is electrostatically attracted to a anion site where the negative electrical charge is dispersed over a few neighboring oxygens on the surface. Assume that the weakly attracted molecule is undergoing rapid diffusion about the threefold axis normal to the particular facet facing the surface. This motional model is similar to that of the Lewis site ammonia species except that the three diffusing "facial" deuterons are facing the surface (upside down relative to the Lewis site species). Additionally an "apical" hydrogen site (which is the fourth hydrogen site located on the threefold axis) is present. The reorientation of the ammonium ion may involve such a hypothetical species where this motional axis is undergoing a random exchange with another of the three remaining tetrahedral threefold axes. This may be envisioned as a tumbling of the NH_4^+ tetrahedron onto another one of its four facets by a thermal process like translation over the surface. As the sample temperature is decreased, the thermal energy available to the hypothetical system will ultimately fall below the activation energy for this tumbling process (see Figure 11).

To determine what line shapes would result from the hypothetical motional model described above, ^2H quadrupolar spin-echo simulations were generated.[30] These line-shape simulations calculate the observable magnetization of a nucleus (spin $I = 1$) after performing a quadrupolar spin–echo experiment and account for finite pulse power.[22] These calculations include the effect of random reorientation (which is treated as a stationary Markov process[31]) during the time of the spin–echo and acquisition. The

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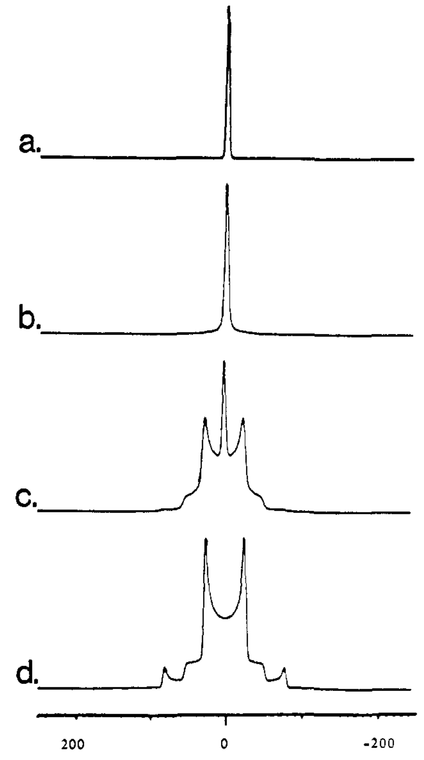

Figure 12. ^{2}H quadrupolar spin-echo simulation spectra for the motional model proposed for the Brønsted species, 40-μs echo delay: (a) $k_{af} = 10^8$ Hz, (b) $k_{af} = 5 \times 10^4$ Hz, (c) $k_{af} = 10^4$ Hz, (d) $k_{af} = 0$ Hz.

simulated time domain information is subsequently Fourier transformed yielding the line shape for the given model.

The specification of the motional model requires the number and relative orientation of the jump sites, the a priori population probabilities for these jump sites, and the transfer rates between each of the sites. For the simulations, the four tetrahedral sites were given equal population probability as is dictated by the high symmetry of this system. The three motionally equivalent facial sites were allowed to undergo rapid exchange ($k_{ff} = 10^8$ Hz). A series of simulations were performed in which the exchange rate for a facet site going to the apical site (k_{af}) ranged from 0 to 10^8 Hz. In the range of 5×10^5 Hz or greater, the line shape is observed to be isotropic (Figure 12a). Below 5×10^5 Hz, a 54-kHz ($\eta = 0$) Lewis-like component begins to emerge (Figure 12b) and ultimately dominates the resonance (Figure 12c). For a k_{af} value of 0 Hz, the apical site is disconnected from the facial sites and two independent resonances result: the 54-kHz ($\eta = 0$) resonance from the motionally averaged facial deuterons and a 162-kHz ($\eta = 0$) resonance due to the unaveraged apical deuteron, with a spectral area ratio of 3:1, respectively (Figure 12d). The simulations indicate some dependence of the line shape upon the value of τ_{qe} for the intermediate k_{af} value (5×10^5 Hz; figure not shown). Specifically the isotropic resonance undergoes some narrowing at the base for increasing values of τ_{qe}. However, this dependence is quite minor and would be obscured by the other resonances in experimental spectra.

The preceding model for the motion of ammonium ions serves to explain the temperature dependence of ND$_3$/PDA ^{2}H NMR spectra. Some details of the mobility of the ammonium species remain uncertain. It may involve a localized surface species (such as an ammonium molecule which is associated with one or a few hydroxyl sites) and/or a highly mobile ammonium species which is free to undergo translation across the surface. The survival of the quadrupolar interaction suggests a localized surface species. The constrained mobility of ammonia on γ-alumina is also supported by previous experimental thermodynamic calculations.[8b] The continuous transition of the isotropic component in the variable-temperature experiments (Figure 11) indicates a distribution of reorientational activation energies.

The experimental spectra obtained for ammonia interacting with γ-alumina in this study indicate the presence of a distribution of surface binding sites. This distribution is manifested in the broadening of the ^{15}N resonances (Figure 1) and the rounded discontinuities of the ^{2}H resonances (e.g., Figure 3), and also in the continuity of the line-shape transition in the variable-temperature ^{2}H experiments (Figure 11).

For insight into the nature of this surface heterogeneity, consider some previous investigations of γ-alumina. Alumina surface structures have been modeled by several authors[32] (a comprehensive discussion of these model surfaces was given by Knözinger and Ratnasamy[6]). The general approach was to a consider a polycrystalline γ-Al$_2$O$_3$ sample which is composed of one or a combination of low index oxygen lattice planes [(1,0,0), (1,1,0), (1,1,1)] which correspond to the defect-spinel morphology known for γ-alumina. Beginning with a hypothetical sample saturated with hydroxyl groups (100% monolayer), Monte Carlo calculations[32] were performed to simulate the combination and desorption of hydroxyl groups in the form of water. These simulations show three major hydroxyl site classifications, corresponding directly to the number of Al^{3+} cations to which the hydroxyl oxygen atoms are attached.

Type I hydroxyl sites are attached to only one Al^{3+} cation, type II to two, and type III to three subsurface aluminum ions. Type I hydroxyl oxygens share electron density with only one Al^{3+} atom and have a relatively significant electronic overlap with the hydrogen at that site, making this hydroxyl a relatively weak acid site. Type II hydroxyl sites have intermediate acidity and type III sites have the highest acidity. By the same rationale, type III oxygens are shown to be least likely to undergo desorption, whereas the type I hydroxyl groups are most labile. Further divisions of these three major groups arise according to the site symmetries of the coordinating Al^{3+} (O_h or T_d environment) and also between the various index planes (variations in steric hindrance are invoked here).

These simple arguments for idealized surfaces, when considered with the likelihood of surface defects and the contribution of higher order index planes, give some appreciation of how the spectral heterogeneities observed for the ammonia surface species arise. It is evident from the observed heterogeneities that the use of distribution functions in line-shape calculations may be appropriate, and is currently being investigated in our laboratory.

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Registry No. NH$_3$, 7664-41-7; Al$_2$O$_3$, 1344-28-1.

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