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NMR Studies of Pyridine on Silica-Alumina¹

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Abstract: ¹³C and ¹⁵N NMR spectroscopy with cross-polarization and magic-angle spinning have been used to study the structure and dynamics of pyridine adsorbed on silica-alumina. Hydrogen bonding is shown to be the dominant interaction at high loading levels (0.5 to 1 monolayer). At lower coverages, a Lewis acid-base complex dominates and the pyridine is significantly less mobile. Brønsted complexes are found if the surface has been pretreated with HCl gas; ¹⁵N NMR provides evidence for two distinct protonated forms of adsorbed pyridine. Experiments with variable contact time or with the decoupler off provide evidence for rotational diffusion about the C₂ axis of adsorbed pyridine.

The oxides of aluminum and silicon are catalytically important materials that have been investigated extensively in order to determine the nature of their adsorption sites. Investigations have focused on the following points, among others: the *geometry* of sites (e.g., octahedral and tetrahedral environments of the highly defective spinel structures of the aluminas); the type of bonding between substrate and adsorbate (e.g., physical adsorption whether of nonspecific nature due to dispersion forces or specific due to hydrogen bonding with surface hydroxyls); and the molecular *dynamics* of the adsorbed species (e.g., molecular diffusion and chemical exchange, which are important, for example, in cracking reactions). The use of spectroscopic techniques either singly or in combination has proven to be particularly effective in these investigations and in identifying the types and strengths of acid sites.

Infrared spectra of pyridine adsorbed on alumina and silica-alumina have provided considerable qualitative information on the nature of the interaction of adsorbed pyridine on these surfaces.² Several skeletal vibrational frequencies of pyridine can shift by more than 100 cm⁻¹, the shift depending on the type of adsorption site and interaction, i.e., hydrogen bonding with surface hydroxyls, protonation to form pyridinium ions (Brønsted acid sites), or Lewis acid-base interactions of the nitrogen lone pair with electron-deficient sites.

Despite considerable progress, there remains a need for a better and quantitative definition of the interaction of probe molecules such as pyridine with oxide surfaces, so that a quantitative definition of the adsorption sites may be established. In this paper we describe the use of ¹³C and ¹⁵N magic-angle spinning NMR techniques in the study of a silica-alumina system, specifically as reflected in the adsorption properties of pyridine.

The combination of excellent radio-frequency penetration and surface-selective excitation techniques (e.g., ¹H-¹³C cross polarization) allows surface NMR studies to be made of bulk sam-

ples. The total surface area available for study is limited by particle size, porosity, and the spectrometer's active volume. Because NMR can examine a very large total surface (e.g., ~300 m² in this study), the sensitivity of ¹³C NMR may rival or exceed that of other surface techniques. Furthermore, isotopic enrichment can lower detection limits by 2 orders of magnitude. Most surface-selective spectroscopic techniques require high vacuum and are not useful for the investigation of loosely adsorbed, volatile species. Additionally, signal averaging is often limited by the inherently destructive nature of some surface probes (e.g., X-rays and electron beams). These restrictions do not apply to NMR studies of adsorbed molecules.

In addition to providing information on the acidic sites of the substrate, pyridine as the adsorbed species is particularly important from the methodological viewpoint. The rigid, symmetrical nature of the pyridine molecule greatly simplifies the characterization of the structure and mobility of adsorbed species relative to those of other adsorbed bases that have been studied (e.g., *n*-butylamine³). Pyridine and pyridine derivatives constitute a class of compounds thoroughly studied by nitrogen NMR.^{4,5b} The ¹⁵N chemical shift of pyridine is very strongly dependent on solvent^{5,6} and would, therefore, be expected to be a sensitive probe for interactions with surface sites.

¹³C NMR studies have been reported on a variety of substrate-adsorbate systems.⁸ It has been found that the more mobile or loosely bound adsorbates can be observed directly in

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straightforward Bloch decay (BD) NMR experiments (i.e., pulse Fourier transform) of the type employed routinely for liquid-state studies. The ^{13}C NMR resonances of more tightly bound substrates have much broader lines. For example, Gay and Liang have reported a sharp ^{13}C BD spectrum of pyridine adsorbed on silica but state that only a "single featureless peak" could be obtained at room temperature for pyridine adsorbed on alumina at 28 °C and show a very broad spectrum for pyridine on alumina even at 62 °C.^{8a} This broad-line ^{13}C NMR spectral characteristic is expected of more tightly bound adsorbates because of the manifestation of chemical shift anisotropies and dipolar interactions with protons. These broadening effects can, however, be minimized by magic-angle spinning (MAS)⁹ and high-power ^1H decoupling techniques.¹⁰ The anticipated sensitivity-limiting time bottleneck of long ^{13}C spin-lattice relaxation times can be sidestepped by carrying out the ^1H decoupling with a ^1H - ^{13}C cross-polarization (CP) approach.

Ellis and co-workers have reported a CP/MAS study of pyridine adsorbed on γ -alumina.¹¹ In their study, the estimated surface coverage was one-twentieth of a monolayer. ^{13}C chemical shifts identical within experimental error to solution-state values were reported. We have been carrying out extensive ^{13}C CP/MAS NMR studies of pyridine adsorbed on silica, alumina, and silica-alumina.¹² The present paper is a report on the pyridine/silica-alumina system.

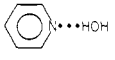
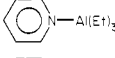
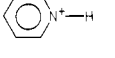
Experimental Section

NMR Spectra. Most of the solid-state ^{13}C spectra (including variable-temperature experiments) were measured at a carbon frequency of 50.3 MHz on a modified Nicolet NT-200 spectrometer equipped with a wide-bore 4.7-T magnet.¹³ Kel-F rotors were used at a spinning speed of 1.6–2.0 kHz. Additional solid-state spectra were measured at a carbon frequency of 15.0 MHz on a modified JEOL FX-60QS spectrometer;¹⁴ Kel-F rotors were used at a spinning speed of 2 kHz. All room-temperature MAS spectra were obtained using home-built probes; variable-temperature spectra were obtained with a probe obtained from Chemagnetics, Inc. All solid-state ^{13}C spectra were externally referenced to liquid tetramethylsilane (Me_4Si) based on substitution of hexamethylbenzene (HMB) as the secondary reference and assigning 132.3 and 16.9 ppm to the shifts of the aromatic and aliphatic carbons, respectively, of HMB relative to liquid Me_4Si . All solution-state ^{13}C spectra were measured at 25 MHz on a JEOL FX-100Q spectrometer.

All solid-state ^{15}N spectra were measured at a ^{15}N frequency of 20.3 MHz on a modified Nicolet NT-200 wide-bore spectrometer.¹⁵ Kel-F rotors were again used, with a spinning speed of 2.5 kHz. All ^{15}N chemical shifts were externally referenced to liquid ammonia, based on substitution of a saturated aqueous solution of ammonium nitrate as the secondary reference and assigning 20.7 ppm to the shift of the ammonium nitrogen of ammonium nitrate relative to liquid ammonia.^{5a}

The cross-polarization/magic-angle spinning experiment has been described previously,⁹ but since the pyridine/silica-alumina spectra differ in significant ways from spectra of rigid solids, a short discussion is appropriate. Magic-angle spinning is used to average the chemical shift anisotropy (CSA) of each spin to an isotropic value. If the spinning speed of a rigid solid is not greater than the magnitude of the CSA, spinning sidebands are observed. High-power proton decoupling is used to remove ^{13}C - ^1H dipolar coupling. In rigid, diamagnetic solids ^{13}C line widths are on the order of 10 kHz in the absence of dipolar decoupling. Rapid isotropic motion in nonviscous liquids efficiently removes both of the

Table I. ^{13}C Chemical Shift Differences for Pyridine/Silica-Alumina^a

sample coverage ^b	fractional coverage ^c	α - β	α - γ	remarks
1.51	0.82	24.2	11.3	Figure 4c
1.02	0.55	23.9	10.8	Figure 1a
0.38	0.21	22.7	8.8	Figure 1b
0.17	0.09	21.3		spectrum not shown; γ peak not well determined
1.2 (0.31 g of HCl)	0.65	19.9	4.8	Figure 1c
liquid pyridine		26.3	14.3	ref 17
		25.1	12.8	obtained from solution data (this work)
		21.6	6.9	obtained from solution data (this work)
		15.1	-4.3	obtained on solid pyridinium sulfate (15.1 and -4.3 ppm solution data, ref 17)

^a Chemical shift differences in ppm. ^b g of pyridine/10 g of silica-alumina. ^c Estimated from sample coverage by using the model described in the text.

above line-broadening mechanisms. If loosely adsorbed surface species have significant mobility, motion can reduce CSA and dipolar couplings. Such reductions can lower the spinning speed necessary for the elimination of spinning sidebands and make possible the observation of signals in the absence of high-power decoupling.

Bloch decay spectra (^{13}C pulse, data acquisition followed by a delay to allow ^{13}C magnetization to return) were obtained at 25.1 MHz with a JEOL FX-100Q spectrometer without magic-angle spinning or high-power ^1H decoupling. Such spectra are expected to yield sharp lines of mobile components exclusively.

Materials. The silica-alumina was a 75% SiO_2 -25% Al_2O_3 (weight percent of the oxides) system obtained from American Cyanamid, with a surface area of 485 m^2/g .¹⁶ Samples were prepared by heating the substrate at 160 °C and 10^{-4} torr for 24 h and then at 25 °C adsorbing pyridine (or ^{15}N -enriched pyridine) at its vapor pressure at 25 °C up to a prescribed loading level determined by the amount of pyridine employed. Two silica-alumina samples were treated with HCl gas at 25 °C prior to adsorption of pyridine, but otherwise prepared as above. The following procedure was used with the intent of preparing samples in which the pyridine was exclusively chemisorbed. A sample of silica-alumina was evacuated at 160 °C for 18 h. After cooling to room temperature, the sample was exposed to 10 torr of pyridine. The sample was heated at 160 °C for 3 h followed by evacuation for 50 min at 160 °C.

Results and Discussion

^{13}C chemical shift data for the pyridine/silica-alumina systems are summarized in Table I. Since protonation and complex formation are known to produce different changes in chemical shift¹⁷ for different carbons (e.g., α , β , and γ) in pyridine, and as external referencing is subject to possible errors, these data are reported in terms of intramolecular ^{13}C chemical shift differences (α - β and α - γ). Also shown are ^{13}C chemical shift differences for relevant model systems. The fractional monolayer coverages given in the tables were estimated by assuming a model in which the pyridine is attached to the substrate at its nitrogen atom and sweeps out a cylindrical volume normal to the surface because of rotation about the C_2 axis through the nitrogen and γ carbon atoms. Such motion implies a significant anisotropy in the time dependence of the ^{13}C - ^1H dipolar interactions responsible for the cross polarization of the α , β , and γ carbons of pyridine. In the calculation of the effective surface area swept out by an adsorbed pyridine molecule, a molecular radius of 3.3 Å, which includes a 1.2-Å contribution from the van der Waals radius of the hydrogen atom, was used. This calculation yielded an area of 34.4

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(12) Preliminary results for the pyridine/ γ -alumina system obtained in our laboratory differ significantly from those reported by Ellis and co-workers. Further work is under way to resolve this discrepancy.

(13) Typical experimental parameters: 1-ms contact time, 5000–30 000 1-s repetitions, 10-G ^1H decoupling field.

(14) Typical experimental parameters: 1-ms contact time, 10 000–50 000 1-s repetitions, 12-G ^1H decoupling field.

(15) Typical experimental parameters: 1-ms contact time, 50 000 1-s repetitions, 12-G ^1H decoupling field.

(16) Determined by the nitrogen BET method.

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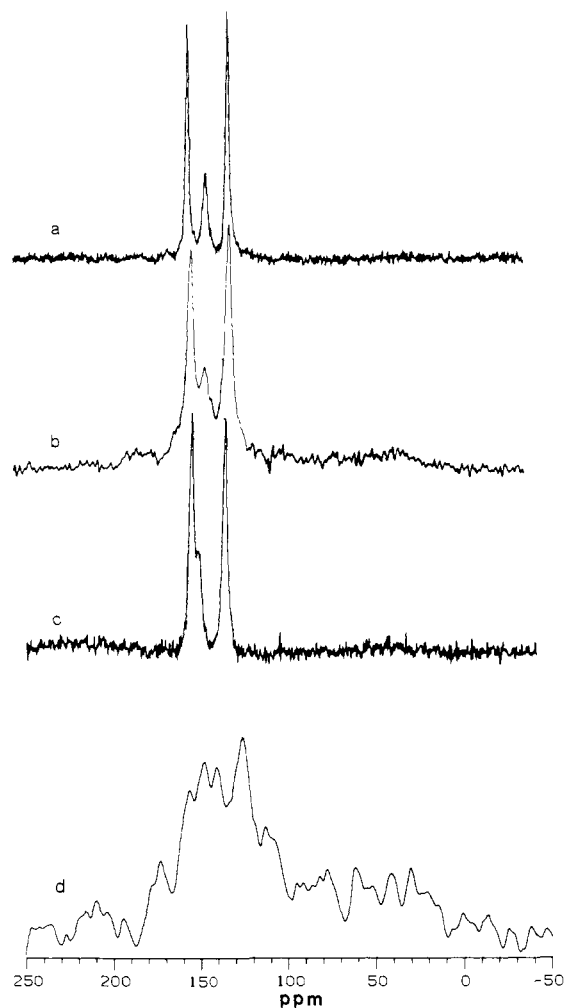


Figure 1. 50.3-MHz ^{13}C CP/MAS spectra of pyridine adsorbed on silica-alumina: (a) 1.02 g of pyridine/10 g of silica-alumina; 50 000 1-s repetitions, 1-ms contact time. (b) 0.38 g of pyridine/10 g of silica-alumina; 225 000 1-s repetitions, 1-ms contact time. (c) 1.2 g of pyridine, 0.31 g of HCl/10 g of silica-alumina; 66 000 1-s repetitions, 1-ms contact time. (d) Similar to sample in (a) but heat treated for 3 h at 160 °C and then evacuated; 96 000 0.5-s repetitions, 1-ms contact time, 200-Hz line broadening. The high-shielding region of (d) shows a broad, low-intensity signal that we believe to be due to a contaminant introduced with pyridine by the vacuum system. The intensity of this signal is not reproducible and not related to the duration of sample heating.

\AA^2 per adsorbed pyridine molecule. In studies of pyridine adsorbed on oxide surfaces by other workers, values of 26 $\text{\AA}^2/\text{molecule}^{11}$ and 40 $\text{\AA}^2/\text{molecule}^{18}$ were used to calculate monolayer coverage. The models used to arrive at those values were not reported.

^{13}C CP/MAS spectra (50.3-MHz) for several pyridine/silica-alumina loading levels are shown in Figure 1. Bloch decay spectra (25.1-MHz) are shown in Figure 2. Figure 1a is the CP/MAS spectrum of 1.2-g pyridine/10-g silica-alumina sample; a surface coverage of 0.65 monolayer was estimated for this sample. The Bloch decay spectrum of a 1.51-g pyridine/10-g silica-alumina sample (Figure 2a) has the relatively sharp features characteristic of liquid-like molecules and crystalline solids. Because ^{13}C T_1 values in rigid solids are typically very long, the ease of obtaining a Bloch decay spectrum is evidence for substantial mobility of the adsorbed pyridine. The observation of a CP spectrum for this sample (not shown, chemical shift data in Table I) shows that the motion of the adsorbed pyridine must have an anisotropic component to it, a necessary condition for cross polarization of spins in highly mobile environments. The chemical shift differences in the two spectra are identical, suggesting that

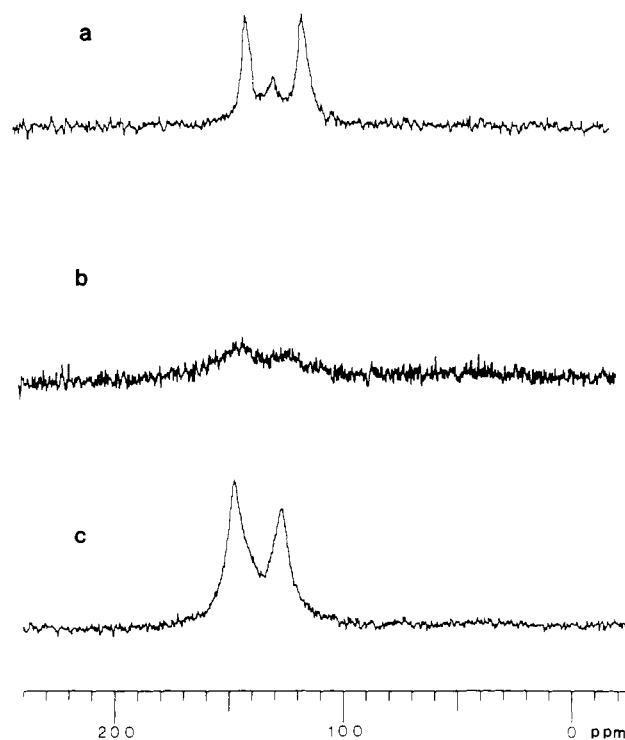


Figure 2. 25-MHz ^{13}C Bloch decay spectra of pyridine adsorbed on silica-alumina: (a) 1.51 g of pyridine/10 g of silica-alumina; 78 000 0.5-s repetitions. (b) 0.38 g of pyridine/10 g of silica-alumina; 83 000 0.7-s repetitions. (c) 1.2 g of pyridine, 0.31 g of HCl/10 g of silica-alumina; 98 600 0.5-s repetitions.

either all of the pyridine is in the same environment or that exchange between mobile, loosely held environments (physically adsorbed) and immobile, tightly held environments (chemisorbed) is rapid on the NMR time scale (i.e., the inverse of relevant chemical shift differences—ca. $1/(500 \text{ Hz}) = 2 \text{ ms}$). The difference between physically adsorbed and chemisorbed pyridine is defined operationally: the former is defined as pyridine that can be removed with pumping at 150 °C, while the latter remains on the surface even after such evacuation. Chemisorbed pyridine is also known to be variously bonded on an alumina surface, with some pyridine remaining chemisorbed even after evacuation at 500 °C; this indicates a range of bond strengths for the interaction between pyridine and the alumina surface.¹⁹ It is expected that the mixed silica-alumina surface should also present a wide spectrum of bonding situations.

The chemical shift differences for these samples compare very favorably with the values for hydrogen-bonded pyridine. It is not surprising that the majority of the pyridine molecules seem to be weakly adsorbed at hydrogen-bonding sites (presumably >Si-OH) at these relatively high levels of loading. Strong adsorption at Al Lewis acid sites is also present, but these sites are saturated at a much lower pyridine coverage (vide infra), and pyridine adsorbed at these sites can contribute only a minor perturbation of the spectra obtained for high loading.

Figures 1b and 2b are the CP/MAS spectrum and Bloch decay spectrum, respectively, for a pyridine/silica-alumina system with 0.38 g of pyridine/10 g of silica-alumina. This corresponds to an estimated fractional coverage of 0.21 monolayer. The spectra of this low-coverage sample are significantly different from those discussed above for the high-coverage samples. The CP/MAS spectrum (Figure 1b) shows significant changes in chemical shift differences relative to the high-loading sample. Comparison with the reference data of Table I suggests two interpretations. The first possibility is that most of the pyridine in the low-coverage sample exists as Lewis acid-base complexes with Al surface sites. The chemical shift differences are quite consistent with this in-

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Table II. Calculated Fraction of Pyridine Molecules in Lewis Acid-Base Complexes (f_L) and Calculated Fraction of Total Surface Sites That Are Lewis Sites Bound to Pyridine (L_p)

sample coverage ^a	fractional coverage ^b	f_L from α - β shift diff	f_L from α - γ shift diff	L_p ^c
1.51	0.82	0.26	0.24	0.21
1.2	0.65	0.34	0.34	0.22
0.38	0.21	0.69	0.68	0.14

^a g of pyridine/10 g of silica-alumina. ^b Estimated from sample coverage by using the model described in the text. ^c Determined from the average f_L obtained from α - β and α - γ shift differences.

terpretation. The second possibility is that a given pyridine molecule is loosely adsorbed roughly 70% of the time and is protonated (i.e., in Brønsted complexes) approximately 30% of the time, exchanging between the two environments at a rate rapid on the NMR time scale. The first possibility implies a relatively immobile environment for pyridine. The second possibility implies substantial mobility, as in the high-loading sample, and can be ruled out by the near absence of a Bloch decay signal for this sample (Figure 2b). This spectrum (2b) implies that nearly all of the pyridine is in a low-mobility environment in the low-coverage sample. We conclude that most of the pyridine is chemisorbed at Lewis acid sites in this sample.

The chemical shift differences in Table I can be used to estimate the relative populations of hydrogen-bonded pyridine and pyridine in Lewis acid-base complexes. This is possible since the chemical shift of a spin involved in a rapid, two-site exchange process is a population-weighted sum of the chemical shifts of the individual, nonexchanging forms. The ¹³C chemical shift differences for pyridine-water and pyridine-Al(Et)₃ (Table I) were used as benchmark values for hydrogen-bonded pyridine and pyridine in a Lewis acid-base complex, respectively. The α - β and α - γ chemical shift differences provide independent measures of the relative populations of the hydrogen-bonded and Lewis acid-base forms.

A possible problem with these calculations is the use of solution-state model complexes. Future studies with substrates of diverse Si/Al ratios could provide more reliable measures of benchmark chemical shift differences. The model used in these calculations also assumes that hydrogen bonding and Lewis acid-base complexation fully account for the adsorption of pyridine at coverages less than one monolayer on untreated silica-alumina. This is consistent with infrared data, on the basis of which it has been concluded that the primary acidic sites on silica-alumina are Lewis type centered on trigonal aluminum atoms and that the apparent Brønsted acidity results from the interaction between a molecule adsorbed on a Lewis site and a surface hydroxyl attached to an adjacent silicon atom.²⁰

Calculated values of the fraction of adsorbed pyridine molecules involved in Lewis acid-base complexes (f_L) are tabulated in Table II for three levels of surface coverage. Values calculated from α - β shift differences and α - γ shift differences are in separate columns; the agreement is excellent. These calculations show that, as the pyridine surface coverage decreases, Lewis acid-base complexes have an increasing importance in the description of pyridine adsorption. This result is consistent with reduced pyridine mobility for low-coverage samples.

The fraction of adsorbed pyridine molecules involved in Lewis acid-base complexes can be multiplied by the estimated fractional monolayer coverage to yield an estimate of the fraction of total surface sites which are Al Lewis acid sites complexed by pyridine (L_p). These values are also included in Table II. At pyridine coverages high enough to saturate the Lewis acid sites, these values are expected to be measures of the surface concentration of Lewis acid sites. The calculated values for the two higher coverage samples suggest that approximately 21% of all surface sites available for pyridine adsorption are Lewis acid sites. This value

is in close agreement with the bulk Si/Al oxide ratio stated by the manufacturer.

The calculated fraction of total surface sites that are Lewis acid sites bound to pyridine is significantly lower for the 0.21 monolayer coverage sample, 14%. This suggests a finite equilibrium constant for pyridine exchange between hydrogen-bonding >Si-OH sites and Lewis acid sites. The prospect of determining thermodynamic data for such exchange processes is an intriguing possibility for future, more detailed studies.

Figures 1c and 2c are the CP/MAS spectrum and Bloch decay spectrum, respectively, of a sample prepared by exposing the silica-alumina to HCl gas prior to treatment with pyridine. The sample contained 0.31 g of HCl and 1.2 g of pyridine per 10 g of silica-alumina. The observed chemical shift differences are consistent with rapid exchange between equal amounts of protonated pyridine and nonprotonated, hydrogen-bonded pyridine. This is in good agreement with the extent of protonation predicted from the mole ratio of HCl to pyridine. The observation of a strong Bloch decay spectrum (Figure 2c) with chemical shift differences consistent with those in the corresponding CP/MAS spectrum strongly implies rapid pyridine exchange between protonated and nonprotonated forms. Comparison of spectra b and c in Figures 2 provides further support for the assignment of the 0.38-g pyridine/10-g silica-alumina sample to an immobile, Lewis acid-base complex, rather than a system exchanging between protonated and nonprotonated forms.

Figure 1d is the CP/MAS spectrum of a sample that was heated and evacuated at 160 °C following adsorption of pyridine. Although the signal-to-noise ratio is very poor, the chemical shift differences in Figure 1d are consistent with strong chemisorption, possibly a mixture of Lewis acid-base complexes and protonated forms. The lines are very broad, suggesting an exchange rate near coalescence or inhomogeneous chemical shift differences due to a number of dissimilar adsorption sites with no exchange averaging. A behavior analogous to the latter case has been observed in ²⁹Si NMR studies of rigorously dehydrated silica gel surfaces.²¹ In the absence of exchange averaging, surface heterogeneities (e.g., various crystal faces, lattice defects, and nearest-neighbor effects) manifest themselves in heterogeneous broadening of NMR signals from surface species. Definitive proof of heterogeneous broadening (as opposed to exchange broadening) could perhaps be obtained via a reduced-temperature CP/MAS experiment or in principle via a two-dimensional experiment.²² Such experiments would require higher signal-to-noise ratios than available for this work, e.g., with ¹³C-enriched species. ¹³C isotopic enrichment would be of great value in future studies of heat-treated samples.

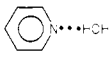
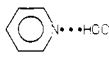
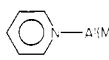
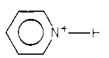
These observations allow several conclusions to be made concerning the motion of pyridine adsorbed on silica-alumina. Loosely adsorbed (e.g., hydrogen bonded) pyridine is apparently able to exchange with chemisorbed pyridine from Lewis acid-base complexes. This rapid exchange results in overall rapid mobility, and Bloch decay spectra are observed for such cases. The CP/MAS spectra show exchange-averaged signals rather than resolved signals from separate motional domains. At low loading levels the pyridine molecules are relatively immobile, and Bloch decay spectra are not observed.

In order to obtain supporting evidence for the above interpretation, a series of samples similar to those discussed above were prepared with 30% ¹⁵N-enriched pyridine, and ¹⁵N CP/MAS spectra were obtained at 20.3 MHz. Table III summarizes ¹⁵N chemical shift data for these samples and for solution-state spectra of appropriate model systems.^{5,7} Figure 3a is the ¹⁵N CP/MAS spectrum of a 1.50-g pyridine/10-g silica-alumina sample. This spectrum shows one sharp signal at a chemical shift of 292.5 ppm. Comparison of this chemical shift with those for the model systems in Table III suggests that hydrogen bonding is the dominant interaction between pyridine and silica-alumina for this sample, in agreement with the conclusions drawn from ¹³C spectral results.

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Table III. ^{15}N Chemical Shifts for Pyridine/Silica-Alumina

sample coverage ^a	fractional coverage ^b	^{15}N chemical shift (ppm) ^c	remarks
1.50	0.82	292.5	Figure 3a
0.50	0.27	279.5	Figure 3b
1.02 (with 0.31 g HCl)	0.55	265 (major signal) 198 (minor signal)	Figure 3c
liquid pyridine		317	obtained from solution data, ref 5b
		296	obtained from solution data, ref 7
		299	obtained from solution data, ref 7
		264	obtained from solution data (this work)
		205	obtained from solution data, ref 5b

^a g of pyridine/10 g of silica-alumina. ^b Estimated from the sample coverage by using the model described in the text.

^c Given in ppm relative to liquid NH_3 .

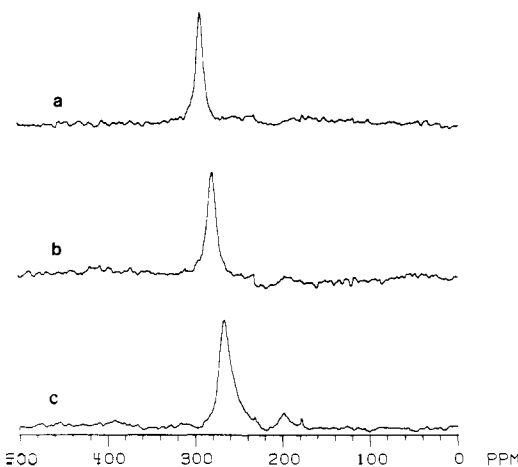


Figure 3. 20.3-MHz ^{15}N CP/MAS spectra of 30% ^{15}N -enriched pyridine adsorbed on silica-alumina: (a) 1.50 g of pyridine/10 g of silica-alumina; 50 000 1-s repetitions, 1-ms contact time. (b) 0.50 g of pyridine/10 g of silica-alumina; 50 000 1-s repetitions, 1-ms contact time. (c) 1.02 g of pyridine, 0.31 g of HCl/10 g of silica-alumina; 50 000 1-s repetitions, 1-ms contact time.

Figure 3b is the ^{15}N CP/MAS spectrum obtained for a 0.50-g pyridine/10-g silica-alumina sample. Again, one main, unstructured peak was observed. The chemical shift of this signal (279.5 ppm) is intermediate between those for neat pyridine and pyridine complexed by the Lewis acid $\text{Al}(\text{Me})_3$, a result consistent with the conclusions drawn from the ^{13}C data. ^{15}N Bloch decay spectra were not attempted, because of the anticipated low sensitivity in this mode of operation.

Figure 3c is the ^{15}N CP/MAS spectrum of an HCl-pretreated sample. This spectrum provides direct evidence for two discrete nitrogen species that interchange slowly (if at all) on the NMR time scale. The most intense signal has a chemical shift of 265 ppm, exactly the average of neat pyridine and protonated pyridine. This is in agreement with the ^{13}C study of a similar sample (Figure 1c), which suggested rapid exchange between protonated and unprotonated forms, with each pyridine protonated approximately half the time. The chemical shift of the low-intensity signal (198 ppm) is suggestive of a fully protonated pyridine species, possibly a nonexchanging Bronsted surface complex. The exact nature of this complex remains speculative. The success of ^{15}N NMR in distinguishing discrete surface species is likely due to the greater

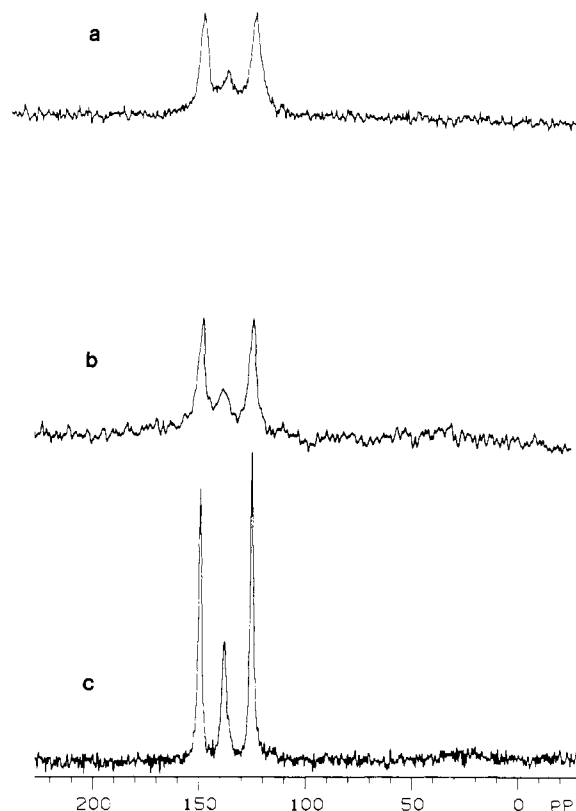


Figure 4. Variable-field ^{13}C spectra of pyridine adsorbed on silica-alumina, 1.51 g of pyridine/10 g of silica-alumina: (a) 25.1-MHz Bloch decay spectrum; 78 000 0.5-s repetitions. (b) 15.0-MHz CP/MAS spectrum; 14 560 1-s repetitions, 1-ms contact time. (c) 50.3-MHz CP/MAS spectrum; 25 000 1-s repetitions, 1-ms contact time.

chemical shift range of ^{15}N and the more direct influence of binding on nitrogen shifts relative to the shifts of the more remote carbons.

The results of the ^{15}N CP/MAS experiments suggest an interpretation consistent with that given above for the ^{13}C experiments. At high surface coverages (0.5 to 1 monolayer) hydrogen bonding dominates the adsorption. High surface coverages promote rapid exchange between hydrogen-bonded species and Lewis acid-base complexes, and a single, exchange-averaged signal is observed. Assuming a higher concentration of hydrogen-bonding sites than Lewis acid sites on the surface, the spectra under these conditions are dominated by the characteristics of the hydrogen-bonded complexes.

A lower limit on the motion of pyridine at high surface coverages can be established. Solid pyridine (at -105°C) is known to have a ^{15}N powder pattern width of 782 ppm.²³ At the relatively modest spinning speed used for the spectrum in Figure 3, an extensive pattern of spinning sidebands would be evident in the absence of efficient motional averaging. The observation of no spinning sidebands sets an upper limit to the residual CSA of 2.5 kHz. CSA values for sp^2 -hybrid ^{13}C spins typically range from 160 to 230 ppm (e.g., 180 ppm for benzene). No spinning sidebands are observed in the ^{13}C CP/MAS spectra, a result consistent with a motionally reduced CSA. The observation of relatively sharp ^{13}C Bloch decay spectra for samples with a high surface coverage implies that the isotropic component of motion for pyridine in those systems is fast relative to the CSA in hertz.

A number of additional ^{13}C experiments were carried out to characterize further the dynamics of adsorbed pyridine. Before interpreting the ^{13}C line widths it is necessary to rule out one possible line broadening mechanism, chemical exchange coalescence. This was achieved for a high-coverage sample (1.51-g pyridine/10-g silica-alumina) by acquiring spectra at three different static magnetic field strengths. The resulting spectra are

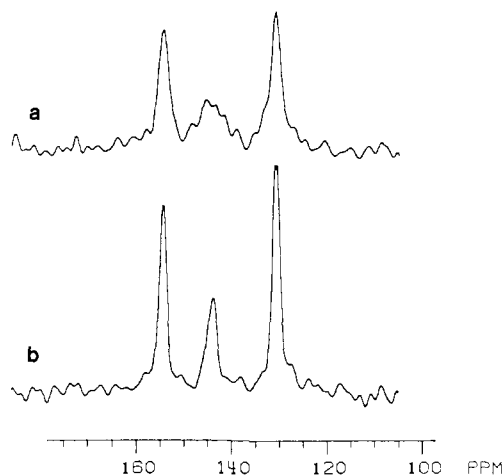


Figure 5. 50.3-MHz CP/MAS spectra of pyridine adsorbed on silica-alumina; 1.5 g of 30% ^{15}N -enriched pyridine/10 g of silica-alumina: (a) with no ^1H decoupling; 8000 1-s repetitions, 2-ms contact time; (b) with high-power ^1H heteronuclear decoupling; 8000 1-s repetitions, 2-ms contact time.

shown in Figure 4. CP/MAS spectra were obtained at 50.3 and 15.0 MHz. The 25.1-MHz spectrum was obtained via Bloch decays and without MAS. An exchange-coalescence line-broadening contribution increases (in hertz) with increasing H_0 . The observation that the line width in hertz is approximately independent of field strength rules out exchange coalescence as a major contribution for broadening at ambient temperature for this sample.

Further support for substantial pyridine mobility at high surface coverages is afforded by the spectra in Figure 5. The 50.3-MHz ^{13}C CP/MAS spectrum of a sample²⁴ consisting of 1.50 g of pyridine/10 g of silica-alumina is shown in Figure 5b; this spectrum was obtained with the decoupler on during data acquisition, the conventional mode of operation. Figure 5a was obtained under identical conditions, except no ^1H decoupling was used during data acquisition. The α and β carbon signals in Figure 5b have line widths of 83 Hz. If ^{14}N - ^{13}C dipolar couplings were not averaged by motion for this sample, the α carbon resonance would be broader than that of the β carbon because of an effect related to the nuclear electrical quadrupole moment of ^{14}N .²⁵ A very modest broadening of the three signals occurs in the absence of decoupling; the increase in line width for the α and β carbons is a mere 47 Hz, yielding line widths of 130 Hz (Figure 5a). This line width is smaller than the magnitude of one-bond ^1H - ^{13}C scalar coupling constants typical for sp^2 -hybrid carbons (~ 160 Hz). The observation that these lines show no hint of a doublet structure suggests that ^1H - ^1H spin-spin flip-flops occur at a rate rapid compared to the scalar ^{13}C - ^1H coupling constant, thus providing a self-decoupling mechanism. This effect has recently been the focus of a study of a hexane-beclomethasone dipropionate inclusion complex in our laboratory.²⁶

The observation that the line width is increased a mere 47 Hz is a MAS experiment by turning off the ^1H decoupler is consistent with the view that the reorienting motion of pyridine on the surface must be both rapid and somewhat anisotropic; this is the view put forth to explain the absence of spinning sidebands in the normal CP/MAS spectra. MAS is able to average inhomogeneous ^{13}C - ^1H dipolar couplings. Inhomogeneous behavior in such couplings requires the absence of the rapid ^1H - ^1H flip-flops that result from strong ^1H - ^1H dipolar couplings. Molecular motion reduces the effective ^1H - ^1H dipolar couplings, thereby reducing the rate of ^1H - ^1H flip-flops. Hence, the failure to observe scalar couplings

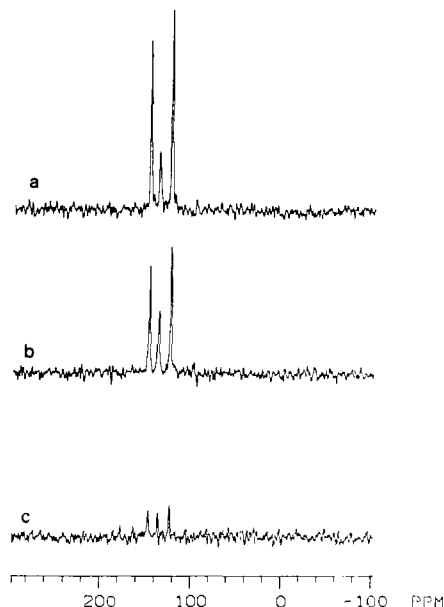


Figure 6. Variable contact-time 50.3-MHz CP/MAS spectra of pyridine adsorbed on silica-alumina, 1.5 g of 30% ^{15}N -enriched pyridine/10 g of silica-alumina: (a) 5-ms contact time, 16 000 1-s repetitions; (b) 1-ms contact time, 16 000 1-s repetitions; (c) 200- μs contact time, 16 000 1-s repetitions.

implies that some resultant ^1H - ^1H dipolar coupling is present. If the magnitude of the ^{13}C - ^1H interaction (roughly 10^4 Hz in a static molecule) is greater than the spinning speed (in this case 1.8 kHz) and the interaction is inhomogeneous, a pattern of dipolar spinning sidebands should be observed. The observation of relatively narrow lines and no sidebands in the decoupler-off experiment implies that the isotropic component of motion must have a rate comparable to the size of static ^{13}C - ^1H dipolar couplings (10^4 Hz) and that the residual ^{13}C - ^1H coupling must be less than the sample spinning speed (1.8×10^3 Hz).

The γ -carbon signal of pyridine is 3 times broader in the decoupler-off experiment than in the conventional spectrum (330 Hz vs. 110 Hz). Preferential broadening of the γ carbon by ^1H - ^{13}C dipolar interactions is consistent with an anisotropic component to the overall motion of adsorbed pyridine (vide infra). There is evidence that pyridine adsorbed (either strongly or loosely) on such polycrystalline oxide systems undergoes anisotropic motion. For example, an early study of pyridine adsorbed on modified aluminas²⁷ showed that chemisorbed pyridine at temperatures below -110°C was rotating about the C_2 axis at a rate higher than 2 kHz, since the expected intermolecular second moment of the rigid pyridine was reduced to a value of 4.3 G^2 . At temperatures higher than -110°C additional intramolecular motions set in, since the line width narrows from 5.0 to 3.5 G (and the second moment from 4.3 to 2.5 G^2). These additional motions are probably librational in nature, but there is no generalized tumbling.

Cross-polarization dynamics is a useful probe of anisotropic motion. Figure 6 is the stack plot obtained from a variable contact time study of a pyridine/silica-alumina sample with a high loading level. The relative intensity of the γ carbon decreases with increasing value of the contact time. This is consistent with anisotropic motion of pyridine favoring rapid rotation about the C_2 axis. This mode of rotation creates no averaging of the ^{13}C - ^1H dipolar coupling for the γ carbon. The ^{13}C - ^1H bond vectors for the α and β carbons are at angles of 60° with respect to the C_2 axis, an angle close to the magic angle (54.7°). Rapid motion about the C_2 axis would be expected to be effective in averaging ^{13}C - ^1H dipolar couplings for the α and β carbons, but not for the γ carbon.²⁸ The observation of a ^{13}C NMR resonance for the

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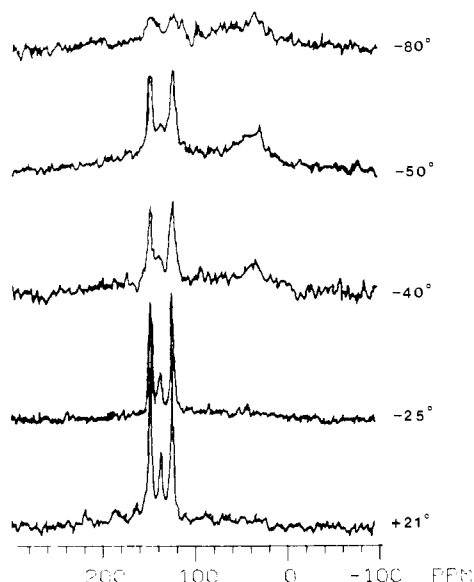


Figure 7. Variable-temperature 50.3-MHz ^{13}C CP/MAS spectra of pyridine adsorbed on silica-alumina; 2000 to 20 000 1-s repetitions per spectrum, 1-ms contact time.

γ carbon in experiments without ^1H decoupling during data acquisition implies that other types of motion reduce the dipolar coupling for this carbon as well. The variable contact time experiment suggests that rotation about the C_2 axis is a significant contribution to a complex overall motion. These results and interpretations are consistent with preferential broadening of the γ -carbon signal in the decoupler-off experiment (Figure 5).

A variable-temperature study was made to explore further the pyridine/silica-alumina system. A high level of loading was again used. Spectra, shown in Figure 7, were obtained from 21 to -80°C . The broad, high-shielding signal is due to vacuum line contamination. As the temperature was lowered, the pyridine lines were observed to broaden. Two general types of mechanisms can account for this observation. According to one, molecular motion on the millisecond time scale can interfere with averaging of MAS and/or ^1H decoupling, producing line broadening.²⁹⁻³¹ Since no

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spinning side bands are observed, even at low temperatures, the motionally reduced CSA must remain smaller than the spinning speed; this implies that molecular motion does not interfere with averaging of the CSA. The possibility of motion interfering with decoupling is not as easily dismissed. A more plausible explanation for the increased line width at low temperature is a decrease in chemical exchange rates, approaching coalescence at -80°C . If this is the case, then further decreases in temperature will not yield well-resolved lines until the temperature is low enough to reduce the exchange rates well below coalescence values. Future experiments at lower loading levels, using ^{13}C -enriched adsorbate, and low temperature may be capable of sorting out the individual species. Such species and equilibria have been discussed before in the interpretations of other types of data.^{27,32}

In summary, the combination of ^{13}C and ^{15}N spectroscopy has provided a relatively detailed characterization of the pyridine/silica-alumina system. The data suggest that hydrogen bonding is the dominant interaction for samples with surface coverages of above 0.5 monolayer. The pyridine is very mobile for loading levels this high, and signals from an exchange-averaged species are observed. Rotation about the C_2 axis is one facet of a complex overall motion. ^{13}C spectral evidence suggests that a low-mobility Lewis acid-base complex dominates at lower loading levels. ^{15}N CP/MAS NMR (of enriched samples) provides evidence for two discrete forms of protonated pyridine for HCl pretreated samples. A further indication that ^{15}N NMR is a more promising probe for adsorbed amines than ^{13}C NMR is the fact that some pyridine samples with much higher isotopic enrichment than the 30% used in this work show additional low-intensity ^{15}N peaks, including a signal at 200 ppm, which may be due to slowly exchanging (or nonexchanging) Brønsted complex. The ^{15}N approach is now under further study.

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Registry No. Pyridine, 110-86-1.

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$X\alpha$ Calculations of the EPR Parameters of Pseudotetrahedral Copper(II) Complexes

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Contribution from Istituto di Chimica Generale, Facoltà di Farmacia, Università di Firenze, and I.S.S.E.C.C., C.N.R., Florence, Italy. Received January 31, 1983

Abstract: The self-consistent-field multiple-scattering $X\alpha$ method has been used to calculate the electronic structure of pseudotetrahedral and square-planar CuCl_4^{2-} ions, with the aim of checking the reliability of the method in the calculation of the spectral (electronic and EPR) properties of transition metal complexes. Several different calculation schemes were used in order to improve the fit to the experimental spectral transitions. Overlapping spheres were found to give the best agreement. The values of g and of the ^{63}Cu hyperfine constant were satisfactorily reproduced, showing that the low value of the latter in the pseudotetrahedral ion is due to covalency effects and not to 4p metal orbital mixing into the ground state.

Introduction

The self-consistent-field multiple-scattering $X\alpha$ (SCF-MS- $X\alpha$) method¹ is widely employed for the calculation of the electronic

structure of transition metal complexes.²⁻⁸ The main advantages of the method lie in the limited computer time required for the

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