

Measurement of Surface Acid Site Concentration by Carbon-13 NMR

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A method of measuring simultaneously the concentration of surface proton and Lewis acid sites is proposed. The method is based on ^{13}C NMR spectroscopy of a suitable adsorbed amine. An investigation of several alkyl-substituted pyridines shows 4-ethylpyridine to be the most satisfactory choice. The method is tested on a silica-alumina cracking catalyst, and found to give good results for total acid concentration. Decomposition of the total acid into proton and Lewis acids requires a higher precision of measurement than presently achieved, but appears possible with existing instruments. Application of the method to silica-alumina with added water shows that the catalyst behavior in the presence of water is more complicated than assumed by previous workers.

INTRODUCTION

It has long been recognized that acidic catalysts may contain both protonic and Lewis acid sites (1). In order to understand the catalytic role of these surfaces it is desirable that the concentration of both types of site be measurable. There exist many methods by which the total surface acid concentration may be obtained (2). Perhaps the most popular of these has been the amine titration method (3), although the ability of this method to give acid strength distributions has recently been challenged (4). The only generally satisfactory method of distinguishing proton and Lewis acids has been the infrared spectroscopy of adsorbed amines, notably pyridine (1, 5). Since the bands due to H-bonded pyridine, coordinated pyridine, and pyridinium ion are distinct (1), this provides a simple method of demonstrating the presence of these sites upon the surface. As a quantitative technique, infrared is less easy, since it requires first, accurate intensity measurements, and second, that the relative extinction coefficients of the surface species be known. In general, there is no way to determine these independently, and it is often necessary to extrapolate from mea-

surements in nonsurface systems. An alternative approach is to assume (5) that addition of H_2O to the surface will convert Lewis sites quantitatively to protonic acids on a one-to-one basis. This permits a calibration of the relative extinction coefficients, but does not permit an independent check on the mode of interaction of the water with the surface.

In a previous publication (6), we have shown that it is possible to obtain ^{13}C NMR spectra from amines adsorbed on acidic surfaces. We found that there is only one resonance line for each carbon, and that the chemical shifts of these lines are a function of the amount of adsorbed amine. These observations may be interpreted on the assumptions that individual amine molecules exchange rapidly on the NMR time-scale between acid and nonacid sites, that the acid sites are always fully occupied, if sufficient amine is present, and that the observed chemical shift is the weighted average of shifts of amine molecules on acid and nonacid sites.

In a subsequent publication (7), we showed that these assumptions are valid for the simple case of HCl on SiO_2 , and further showed that the chemical shifts of adsorbed pyridinium ion agree with those measured

in aqueous solution. Thus in the simplest case, we can write for the observed chemical shift

$$\delta_{\text{obs}} = f_A \delta_A + (1 - f_A) \delta_n \quad (1)$$

where δ_{obs} is the observed chemical shift, δ_A is the chemical shift of an amine bonded to an acid site, δ_n is the shift of an amine on a nonacid site, and f_A the fraction of amine molecules bound to acid sites. Thus if δ_{obs} is measured, a knowledge of δ_A and δ_n permits a calculation of the fraction of amine bound at acid sites. If the total amount of adsorbed amine is known, the total amount bound at acid sites is then obtained. If the acid sites are assumed to be fully occupied, in the case where excess amine is present, this latter figure gives the total concentration of acid sites on the surface.

If the amine can bind to both H^+ and Lewis acids, Eq. (1) may be generalized to

$$\delta_{\text{obs}} = f_H \delta_H + f_L \delta_L + (1 - f_H - f_L) \delta_n \quad (2)$$

where the subscripts H and L refer to H^+ and Lewis acid sites, respectively, and the other symbols have the same meanings as in Eq. (1). In Eq. (2) there are now two unknowns, f_H and f_L , so that if the shift of a single line is studied, only the total acid concentration may be extracted. However, if an amine is studied which has at least two resonance lines, and the ratio of δ_H to δ_L differs for these lines, then an equation of the form of (2) may be written for each line, and the equations solved simultaneously to give the concentration of each type of acid. The success of this decomposition will depend on the finding of a suitable amine, i.e., one with a reasonable difference in shift behavior upon interaction with the two types of acid. It will prove convenient to set $X = f_L + f_H$, $Y = f_L - f_H$ and to rewrite (2) in the form

$$2\delta_{\text{obs}} = X(\delta_H + \delta_L - 2\delta_n) + Y(\delta_L - \delta_H) + 2\delta_n \quad (3)$$

It was shown in (7) that it is satisfactory to use the value measured in aqueous solution for δ_H . In the present work we use the

shift observed for the amine- BF_3 complex as a measure of δ_L . In (6) we showed that δ_n can in principle be obtained from measurements at different coverages. In the present work we use instead the value observed on SiO_2 , which is generally considered (1, 6) not to have acid sites, but which should have similar hydrogen-bonding properties to the silica-alumina catalyst studied.

MATERIALS

The catalyst studied was a silica-alumina cracking catalyst, Davison type 980, which contains 25 wt% Al_2O_3 . The manufacturer's analysis shows the major impurities to be 0.04% Na_2O and 0.05% Fe_2O_3 . The catalyst was received as $\frac{3}{16}$ -in. pellets. These were calcined in air at $500^\circ C$, then ground, and the 80-120 mesh fraction used for investigation. The dry catalyst had a surface area of $400 \text{ m}^2/\text{g}$ as measured by the BET method with N_2 . The catalyst powder was stored in a moist atmosphere, and vacuum degassed at various temperatures immediately before use.

The amines used were obtained from various suppliers. Those showing dark coloration were distilled, and all were dried over molecular sieve. None of the amines showed impurities at the 1% level as determined from ^{13}C NMR of the neat liquids. BF_3 and NH_3 were obtained from Matheson of Canada Ltd., and were vacuum distilled before use.

EXPERIMENTAL

Samples of catalyst with adsorbed amine were prepared using a system comprising an NMR tube and an amine sample bulb connected by a Teflon stopcock. Both the tube and the bulb could be independently attached to a vacuum line for degassing. A measured amount of catalyst (about 1 g) was placed in the NMR tube, degassed overnight at the temperatures noted below, and then sealed off from the vacuum line. A measured amount of amine was then placed in the bulb, frozen, and degassed. This bulb

was then also sealed off from the vacuum line. The stopcock connecting the amine and the catalyst was opened, and the whole apparatus placed in an oven at 90°C for at least 1 hr, and then allowed to cool slowly. The amine used has appreciable vapor pressure at this temperature, and in no case did we observe traces of unadsorbed liquid in the system, or any evidence of nonuniform adsorption. Samples with added water were prepared by the same procedure, the desired amount of water being added to the bulb containing the amine.

Samples for determination of δ_H were prepared by dissolving the amine in excess 6 M aqueous HCl. Samples for determination of δ_L were prepared by adding a 10% excess of BF_3 to a solution of the amine in dried benzene.

All NMR measurements were carried out at 25.16 MHz on a Varian XL-100 instrument in fourier-transform mode, using proton noise decoupling. Spectra of adsorbed species were run at 80°C, which gave reasonably narrow lines without distillation of amine out of the sample. Liquid samples were run at 28°C.

Adsorption isotherms for ammonia were obtained by conventional gas-volumetric techniques.

RESULTS AND DISCUSSION

Choice of Amine

Since pyridine has been much used for this type of study, we decided to concentrate upon pyridine and alkyl pyridines, which are known (8, 9) to have large changes of chemical shift upon protonation. An optimum amine would have at least one carbon which reacts differently to proton and Lewis acids, and would have all lines easily observable in the adsorbed state. Since the adsorbed lines will be rather broad, the latter criterion makes it desirable to use only symmetrically substituted pyridines, which have only three lines in the ring carbon region, rather than five. A further criterion is that lines should not

overlap at any degree of interaction with acid. This excludes the use of pyridine itself. For pyridine, C-4 resonates upfield of C-2, but for pyridinium ion, this order is reversed. Thus there is a point of fractional protonation at which these lines overlap, and for adsorbed samples, where lines are broad, the region over which these lines cannot be separately observed may be intolerably wide (7).

With the above considerations in mind, we studied several amines in HCl solution, and as BF_3 complexes. The results are given in Table 1, which gives the shift of the neat amine relative to TMS, and the changes in shift upon protonation and coordination with BF_3 . All results given in the table are measured with external reference and corrected for susceptibility differences. For the free amine and protonated shifts, our data are in reasonable agreement with previous work (8-10), much of which was done on lower field instruments in CW mode. The present results are the first for the BF_3 complexes.

It can be seen from the table that the effect of both types of acids is a large upfield shift at C-2, a large downfield shift at C-4, and a smaller downfield shift at C-3. Smaller shifts of both signs are observed for alkyl substituent carbons. The shifts at C-2 are similar for both H^+ and BF_3 adducts. The shift at C-4, however, is consistently larger for the protonated species, particularly with the 4-alkyl pyridines. This makes it possible that both proton and Lewis acids can be determined, via Eq. (2).

As a result of these data, we have selected 4-ethylpyridine as the most suitable probe molecule for our investigations. 4-Methylpyridine suffers from the line crossing problem noted above, whereas a larger substituent at C-4 causes this carbon to resonate downfield of C-2 even in the free amine. 4-*t*-Butylpyridine has the best line separation of the molecules studied, but we consider the experimental convenience associated with the greater volatility of 4-

TABLE 1
Protonation and Coordination Shifts

Molecule	Carbon	Amine ^a	H ⁺ shift ^b	BF ₃ shift ^b
Pyridine	2	150.3	-8.3	-7.2
	3	124.0	4.4	2.5
	4	135.9	12.0	7.5
4-Methylpyridine	2	150.0	-9.2	-7.9
	3	124.8	3.9	2.1
	4	146.7	15.3	10.1
4-Ethylpyridine	CH ₃	20.6	2.3	0.4
	2	150.2	-9.1	-7.9
	3	123.5	4.1	2.1
	4	152.6	14.5	9.5
	CH ₂	28.3	1.3	0.1
4- <i>n</i> -Propylpyridine	CH ₃	14.5	-0.5	-1.15
	2	150.1	-9.0	-7.6
	3	124.0	4.0	2.0
	4	151.0	14.8	9.2
4- <i>t</i> -Butylpyridine	α -CH ₂	37.3	0.8	-0.1
	β -CH ₂	23.8	-0.4	-0.8
	CH ₃	13.7	0.1	-0.3
	2	149.9	-8.8	-7.5
	3	120.5	4.7	1.2
2,6-Dimethylpyridine	4	159.0	14.3	9.3
	α -C	34.4	2.4	-4.0
	CH ₃	30.4	-0.3	-0.8
	2	157.7	-10.9	0.1
	3	119.9	5.7	6.3
3,5-Dimethylpyridine	4	136.2	17.5	5.0
	CH ₃	24.5	-4.5	-0.8
	2	147.9	-9.0	-7.5
	3	132.4	6.1	3.9
	4	136.7	11.8	7.0
2,4,6-Trimethylpyridine	CH ₃	18.0	-0.6	0.5
	2	157.5	-5.0	-0.7
	3	120.8	5.3	6.3
	4	146.7	14.0	7.4
	2-CH ₃	24.3	-4.7	-1.0
	4-CH ₃	20.6	1.8	-0.3

^a Chemical shifts of amine with respect to tetramethylsilane. Positive shifts are to lower field.

^b Chemical shifts with respect to the corresponding free amine.

ethylpyridine to outweigh this. To obtain estimates of δ_n we measured the chemical shifts of 4-ethylpyridine adsorbed on SiO₂. The shifts were -0.9, 0.7, 1.5, 0.1, and

-0.5 ppm, respectively, for C-2, C-3, C-4, CH₂, and CH₃ with respect to the neat liquid amine.

Ammonia Adsorption

In order to obtain an independent estimate of the number of strong acid sites on the catalyst, we studied the adsorption of ammonia at 100°C. In Fig. 1 are shown the isotherm on a catalyst degassed at 450°C, and the isotherm obtained after pumping 16 hr at 100°C following the first adsorption. These isotherms are parallel within experimental error, and we take their difference, $0.55 \pm 0.05 \mu\text{mole/m}^2$, as a measure of the strong acid site concentration.

If we assume first-order desorption kinetics for ammonia, then in 16 hr pumping, 90% of those molecules will be desorbed whose rate constant for desorption is $4.0 \times 10^{-5} \text{ sec}^{-1}$, and a higher fraction for those having a greater rate constant. Similarly, only 10% will be desorbed for a rate constant of $1.8 \times 10^{-6} \text{ sec}^{-1}$ and lesser amounts for smaller rate constants. If we approximate the rate constant as $(kT/h)\exp(-E/RT)$ where k is Boltzmann's constant, we find that the two rate constants above correspond to activation energies, E , for desorption of 30 and 32 kcal/mole, respectively. Thus, for our pumping conditions, ammonia on sites with $E \leq 30$ kcal/mole will be essentially all desorbed, while that with $E \geq 32$ kcal/mole is essentially all retained. In these conditions, physically adsorbed and hydrogen-bonded ammonia should be removed, while ammonia bound to strong acid sites is retained, and its amount reflected in the lower coverage observed for the subsequent isotherm.

NMR of Adsorbed 4-Ethylpyridine

Spectra were obtained of varying amounts of 4-ethylpyridine on catalyst samples degassed at two temperatures. A typical spectrum is shown in Fig. 2, and the chemical shifts, with respect to the neat

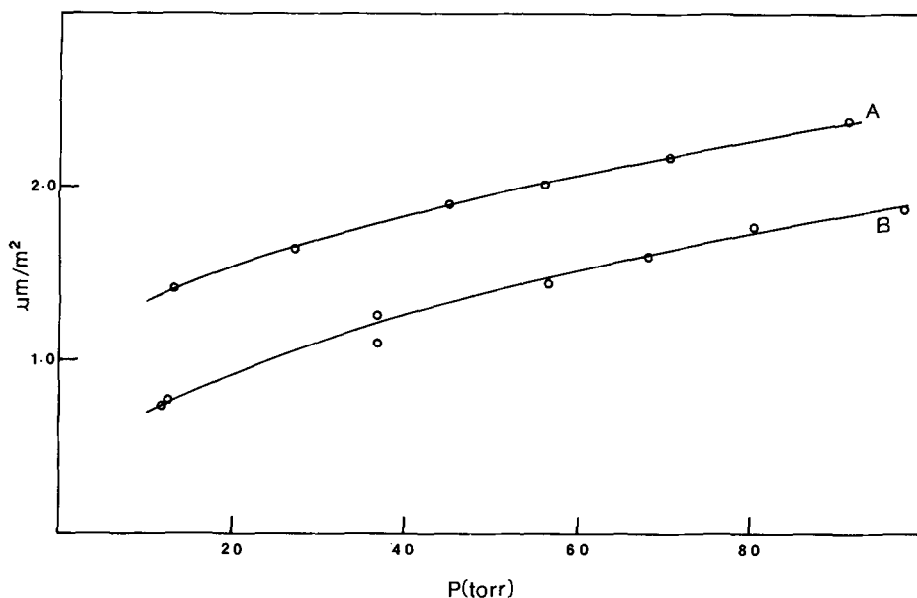


FIG. 1. Adsorption isotherms for ammonia on dry catalyst at 100°C. (A) On catalyst degassed at 450°C. (B) After degassing 16 hr at 100°C, following A.

amine, are collected in Table 2. We estimate from the duplicate sample in the table, and from repeated spectra of the same sample, that the uncertainty in our shift measurements is ± 0.3 ppm.

We now attempt to analyze these data using Eqs. (1) and (3). As a first approximation, we may attempt to find f_A using the C-2 data, where δ_H and δ_i are nearly the same, by averaging these to give a value of -8.5 ppm for δ_A . Solution of Eq. (1) for each sample, and multiplying by the corresponding coverage gives values of n_A , the total

acid concentration, which are reported in the second column of Table 3. Apart from the third point, which clearly contains a gross error, these are reasonably consistent and produce an average of 0.48 ± 0.08 $\mu\text{mole}/\text{m}^2$ for the total acid concentration. This is in good agreement with the value obtained from ammonia adsorption. There is no detectable difference for the two degassing temperatures studied.

We now attempt an analysis for proton and Lewis acid concentrations. To do this, we solve Eq. (3) simultaneously for X and

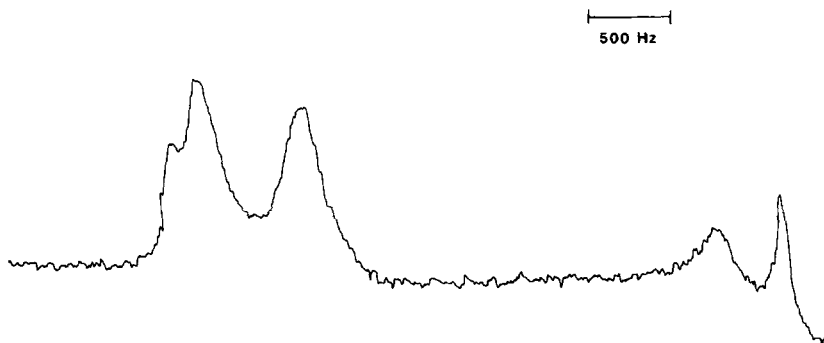


FIG. 2. Spectrum of 4-ethylpyridine on dry catalyst at coverage of $3.22 \mu\text{m}/\text{m}^2$; 10^5 scans at 5 per sec. Temperature, 80°C.

TABLE 2
Chemical Shifts of Adsorbed Amine

Coverage ^a	<i>T</i> ^b	Chemical shifts ^c				
		C-2	C-3	C-4	CH ₂	CH ₃
1.71	270	-3.2	2.5	3.8	1.3	-1.0
2.22	270	-2.2	2.6	3.5	0.4	-1.7
3.22	270	-1.1	1.9	3.1	0.0	-0.8
3.78	270	-2.0	0.7	2.9	-1.8	-1.4
3.78	270	-1.9	0.6	3.3	-1.3	-1.4
2.41	420	-2.9	2.0	4.1	-0.3	-1.8
3.17	420	-2.1	1.2	3.0	-1.2	-1.3
3.78	420	-1.5	1.5	2.5	-0.4	-0.6

^a In $\mu\text{mole}/\text{m}^2$.

^b Degassing temperature in $^{\circ}\text{C}$.

^c In ppm with respect to neat liquid amine.

Y, using both the C-2 and C-4 data. In the obvious manner, these are combined with coverages to produce n_A and n_H , the concentrations of total and proton acid, respectively. These values are shown in columns 3 and 4 of Table 3. It can be seen that the n_A values are again reasonably consistent, producing an average, after discarding the third point, of $0.48 \pm 0.12 \mu\text{mole}/\text{m}^2$. The n_H values, however, are widely scattered, and give an average of $0.2 \pm 0.2 \mu\text{mole}/\text{m}^2$, that is, the present data essentially fail to distinguish the two types of acid site.

It is clear from the above, that data of the present precision allow *X*, the sum of the two types of site to be determined with fair accuracy, but the uncertainty in *Y*, their difference, is unacceptably high. A short calculation shows why this is so. If we assume n_A to be $0.48 \mu\text{mole}/\text{m}^2$ as found above, and consider a coverage of $3.5 \mu\text{mole}/\text{m}^2$, we find from Eq. (2) that the predicted shift at C-4 is 2.6 ppm if all sites are Lewis acids, and 3.3 ppm if all are proton. Given our experimental uncertainty, these are essentially indistinguishable from an equal mixture of the two types of acid. Our lowest coverage points should be slightly better, but not by a great deal.

To improve the accuracy of the decomposition, one would require either a greater

precision of chemical shift measurement, or a smaller ratio of adsorbed amine to total acid site concentration. We do not think that an improvement in shift precision is possible with the present instrument. The accuracy is essentially fixed by the broad linewidth of the adsorbed species. Because of slow motions in the adsorbed phase, C-H dipolar interactions and chemical shift anisotropies are only partially averaged. If a higher field spectrometer were used, the observed shifts would increase while the dipolar interaction remained constant. However the chemical shift anisotropies would also increase, and probably become equal in magnitude to the dipolar coupling in fields of about $7.0 T$. Thus at most about a factor of 2 improvement might be obtained in chemical shift measurement.

It is not feasible to work at substantially lower concentrations than the present, using natural abundance ^{13}C and the present spectrometer. Clearly a big advantage could be gained by isotopic enrichment. For samples, such as zeolites, where the concentration of acid sites may be appreciably higher, the decomposition might succeed at the present precision. The best prospect for improvement, however, is for use of an instrument with improved signal-to-noise ratio. It has been demonstrated

TABLE 3

Calculated Site Concentrations ^a on Dry Catalysts			
Coverage ^b	n_A ^c	n_A ^d	n_H ^d
1.71	0.52	0.58	-0.15
2.22	0.38	0.36	0.31
3.22	0.08	-0.12	1.2
3.78	0.55	0.56	0.14
3.78	0.50	0.42	0.68
2.41	0.63	0.65	0.21
3.17	0.50	0.52	0.11
3.78	0.30	0.27	0.33

^a All values in $\mu\text{mole}/\text{m}^2$.

^b First five samples degassed at 270°C , remainder at 420°C .

^c From Eq. (1) using C-2 data.

^d From Eq. (3) using C-2 And C-4 data.

(11) that the XL-100 can be improved by an order of magnitude in this respect, by using a wide-bore probe. It is also the case that modern high-field spectrometers show a similar gain in signal-to-noise ratio. It would thus be of considerable interest to repeat the present measurements on such an instrument.

Water-Treated Samples

In addition to the above measurements, we carried out a set of experiments in which water was added along with the amine, to produce a fixed water concentration of $3.5 \mu\text{mole}/\text{m}^2$. The experimental results, together with the values of n_A calculated as above from the C-2 data, are shown in Table 4. Some qualitative differences from the dry samples are immediately apparent. Thus the total number of acid sites appears to increase with amount of amine added, and to be in any case greater than the total number of sites found on the dry catalyst. While one can, perhaps, imagine surface structures which would make both protons of an adsorbed water acidic, the apparent increase with amine coverage is more difficult to understand. Experimentally, this increase is manifested as nearly constant chemical shift over the coverage range of 1.1 to $2.8 \mu\text{mole}/\text{m}^2$. This is clearly inconsistent with a model in which a fixed number of acid sites is fully occupied by amine molecules and excess amine enters a state characterized by small shifts. One possibility might be an interaction of the amine with H_2O molecules on the surface. However, since the shifts of pyridine dissolved in water are small (12), this does not seem likely. Perhaps a more likely model would be blocking of acid sites by water molecules, with a competition between free amine and free water for the sites. Clearly this subject needs further study, with varying amounts of adsorbed water. For the present, we suggest that

Coverage ^b	Shifts ^c			n_A ^d
	C-2	C-3	C-4	
0.71	-7.6	3.1	8.9	0.6
1.11	-4.4	1.9	6.5	0.5
1.88	-4.3	2.1	5.5	0.8
2.70	-4.1	1.3	6.2	1.1
2.70	-4.4	1.9	5.4	1.2
2.88	-3.9	1.4	5.3	1.1
3.81	-1.9	1.6	3.9	0.5

^a $3.5 \mu\text{mole}/\text{m}^2$ of added water.

^b In $\mu\text{mole}/\text{m}^2$.

^c In ppm from neat amine.

^d In $\mu\text{mole}/\text{m}^2$, from Eq. (1), using C-2 data.

the assumption of stoichiometric conversion of Lewis to proton sites by water should be regarded with some suspicion.

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