

Competitive Adsorption of Pyridine and Sterically Hindered Pyridines on Alumina

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Infrared observations have been made which show that 2,6-ditertiary-butyl pyridine can displace coordinatively bound pyridine from an alumina surface. Quantitative examination of the displacement of one base by the other has yielded results which lead to the identification of four different adsorption sites on alumina. It is suggested that two of these involve bonding of the base to an electron-deficient oxygen species rather than the hitherto accepted model of coordination direct to an exposed Al^{3+} ion.

Traditionally infrared observations of adsorbed pyridine have been used to characterize Lewis and Brønsted acid sites. Recently Benesi has proposed the use of 2,6-dimethylpyridine as a "reasonably proton-specific" adsorbate in assessing the relative concentrations of the two types of site. However, we have found that 2,6-ditertiarybutyl pyridine (2,6 T) is strongly adsorbed on alumina which is only a weak Brønsted acid.

Infrared studies have been made of the displacement of adsorbed pyridine by 2,6 T and vice versa. In these studies digitized spectra and spectrum accumulation techniques have been used to allow quantitative subtraction of background absorption and reliable determination of difference spectra.

The results indicate clearly that 2,6 T can displace pyridine coordinatively bonded to the surface—a surprising result which indicates that the classical picture for the "Lewis" site of an incompletely coordi-

nated aluminum ion is inadequate. The results of a series of experiments lead to the postulate of four different types of acid adsorption sites on an alumina surface, two of which we believe involve coordination of the base to an electron-deficient oxygen species rather than an Al^{3+} ion. Such an ion would be embedded in the surface and be inaccessible to 2,6 T. It is found also that one of the sites which coordinatively adsorbs pyridine in higher concentration with increasing surface OH concentration cannot adsorb 2,6 T.

INTRODUCTION

In studies of adsorbed bases have been used to investigate the surfaces of alumina and silica-alumina for some years. Comparison of bands in the 1650–1400 cm^{-1} region of adsorbed pyridine with the spectra of the pyridinium ion and various Lewis acid complexes of pyridine showed that Lewis and Brønsted acidity could be readily distinguished (1, 2) on solid surfaces. Further work (3, 4) has put these studies on a firm quantitative basis and

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clarified the band assignments in the 1490 cm^{-1} region.

Studies of adsorbed pyridine, adsorbed ammonia, and the hydroxyl band structure led Peri to propose a model for the alumina surface (5) which has since found wide acceptance. The implications of this model were the absence of Brønsted acidity and the coordination of Lewis-bound pyridine to exposed aluminium ions. The absence of Brønsted-bound pyridine has not been questioned although weak protonic sites have been detected by adsorption of ammonia on alumina dried below 500°C (6).

Substituted pyridines have been used by Knözinger and Stolz (7) to study the effect of base strength on adsorption on alumina. They found that the sterically hindered 2,4,6-trimethyl pyridine was quite strongly bound to "Lewis" sites, being held even after evacuation at 450°C. Benesi, however, suggested (8) that 2,6-dimethyl pyridine (2,6 DMP) could be used as a "reasonably" proton-specific base to yield quantitative measurements of Brønsted and Lewis acidity on acid catalysts. Work on zeolites (9) again using 2,6 DMP indicated that it reacted first with hydroxyl groups and subsequently with Lewis sites.

Brown showed that the only known Lewis acid complex of this latter base (the BF_3 complex) is totally dissociated at 200°C (10). This result suggested that the Lewis acid sites which adsorb 2,6 dimethylpyridine are unusual because of their lack of steric hindrance to the adsorption of the base. The absolute proton specificity of 2,6 ditertiarybutylpyridine (2,6 T) (11) recommended it as an adsorbate for further investigation in this area.

In this work the ir bands for 2,6 T hydrochloride and 2,6 T adsorbed on silica-alumina were used to characterize the bands due to Brønsted acid sites. This information was employed in a study of

the alumina surface where 2,6 T was adsorbed alone and in a series of competitive adsorption experiments. Pyridine and 2,6 T were adsorbed on alumina, dehydrated to differing degrees and the ir spectra recorded before and after addition of the other base.

EXPERIMENTAL

The 2,6-ditertiarybutylpyridine (2,6 T) was from K & K Laboratories, New York. BDH 2,6-dimethylpyridine (2,6 DMP) was fractionated to remove water and pyridine and after distilling from silver nitrate to remove picolines was found to be >99% pure using glc analysis. The Analar grade pyridine was redistilled. All the adsorbates were stored over activated 3A molecular sieve and degassed using several freeze-pump-thaw cycles prior to their use.

The alumina used in the competition experiments was a commercially available gamma-alumina Ketjen 000-3P with a surface area of 250 $\text{m}^2 \text{g}^{-1}$. The samples were in the form of self-supporting 15-mm-diameter disks 15–20 mg in weight pretreated under vacuum at 350°C. The effect of the pretreatment on the surface hydroxyl concentration was monitored by the reduction of the absorption due to the O-H stretch in the 3700 cm^{-1} region. The samples were pretreated for either 1 or 3 hr; more prolonged heating has been shown to give very little further change in the hydroxyl band intensity. A silica-alumina (10% alumina) used for the characterization of the adsorbed 2,6 T was chosen because of its very high surface area (450 $\text{m}^2 \text{g}^{-1}$). It was pretreated at 350°C for 3 hr before the adsorption experiments. A second alumina, Ketjen CK300, which has a surface area of 180 $\text{m}^2 \text{g}^{-1}$ was used to extend the range of these experiments and was pretreated at 500°C for 17 hr.

The BET surface areas were checked using a CI Electronics microbalance which was also used to measure surface coverage of the bases at 0.5 Torr on the alumina.

In the competitive adsorption experiments, 0.5 Torr of base was admitted to the sample at 50°C for $\frac{1}{2}$ hr and then evacuated at this temperature for a minimum of $1\frac{1}{2}$ hr before the second base was added in the same manner as the first. In some experiments 0.5 Torr of each of the bases were added to the adsorbates and their adsorption studied over the temperature range 50–450°C.

The ir cell was constructed to allow the sample to be heated up to 350°C while in the spectrometer beam, silicon windows being directly sealed into the furnace section. The sample disks were mounted in a mild steel holder and maneuvered horizontally into the ir beam and furnace using magnets. The cell was also provided with a furnace arm for treatment temperatures greater than 350°C, which was used only in the experiments where the background was not subtracted. This restriction was necessary because movement of the sample in and out of the ir beam rendered the subtraction questionable.

The ir spectra were recorded using a Perkin-Elmer 257 grating ir spectrometer having a resolution of 4 cm^{-1} at 4000 cm^{-1} and 2 cm^{-1} at 1000 cm^{-1} . The spectrometer was modified to allow automatic repeat scanning of selected regions throughout the range 4000–625 cm^{-1} . An Optilab multianalog 201 logarithmic converter was used to transfer data as absorbance units to a Nicolet Model 1074 signal averaging computer. The computer was used for collection and numerical manipulation of the data which could be drawn out on an x - y recorder. The background spectra of the solids were recorded in the normal manner for the range 4000–625 cm^{-1} and then 32 repeated scans of the 1650–1350 cm^{-1} region were accumulated in the signal averaging computer. Figures 1 and 2 show the way in which the data can be manipulated, subtracting the background spectrum from that obtained after the addition of the base and similarly to

separate the spectrum of the base added second. In this spectrum subtraction, all band intensities which have been decreased by the second adsorption appear as negative bands.

RESULTS

Band Assignments for 2,6 T

Preliminary qualitative experiments, in which 2,6 T was adsorbed on 000.3P alumina, gave rise to a number of bands in the 1650–1400 cm^{-1} region (Fig. 1) which could not be explained in terms of a proton-specific interaction of the substituted pyridine.

Comparison of the spectrum with that of anhydrous 2,6 T hydrochloride which showed a band at 1530.5 cm^{-1} suggested that the 1545 cm^{-1} band was probably assignable to the protonated species. To determine which bands could be unambiguously assigned to the protonated species the competitive adsorption of pyridine and 2,6 T on silica-alumina was investigated. Figure 2 shows clearly the removal of bands at 1547 cm^{-1} and 1495

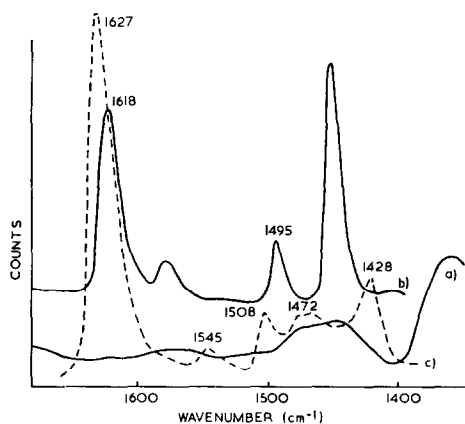


Fig. 1. Adsorption of pyridine and 2,6 T on γ - Al_2O_3 . (a) Background spectrum of outgassed γ - Al_2O_3 . (b) Spectrum of pyridine on γ - Al_2O_3 after evaluation at 50°C with background spectrum subtracted. (c) Spectrum of 2,6 T on γ - Al_2O_3 after evacuation at 50°C with background spectrum subtracted.

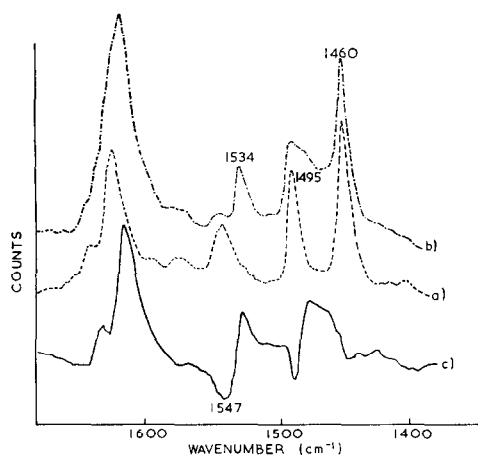


FIG. 2. Adsorption of 2,6 T on silica-alumina in the presence of pyridine. (a) Adsorption and retention after evacuation of pyridine adsorbed at 50°C on silica-alumina. (b) Adsorption and retention after evacuation of 2,6 T on pyridine-treated silica-alumina. (a) and (b) have background γ -alumina spectrum subtracted. (c) Subtraction of (a) from (b) showing negative adsorption bands for displaced pyridine.

cm^{-1} , assigned to pyridinium ion (2, 3), and replacement with bands at 1534 cm^{-1} and 1475 cm^{-1} . The other bands in the spectrum of 2,6 T adsorbed on alumina at 1508 cm^{-1} and 1430 cm^{-1} are seen on

silica-alumina if 2,6 T is adsorbed first, but are removed on addition of pyridine. Table 1 shows the band assignments for pyridine and 2,6 T, the latter generated from these experiments.

Competitive Adsorption Experiments

The Lewis acid sites, on which 2,6 T adsorbs, were investigated by a series of competitive adsorption experiments. The study involved thermally treating two samples of 000-3P alumina for 1 or 3 hr, respectively, and adsorbing first pyridine and then 2,6 T. These two experiments were repeated, adsorbing the bases in the reverse order, attempting to reproduce the levels of dehydroxylation in the first two cases. The results of this series are recorded in two forms, the counts from the multi-channel analyzer in Table 2 and the spectra printed out on the x - y recorder in Figs. 3-5.

The results shown in Table 2 show the counts for the bands assigned to the two bases, adsorbed on Lewis or Brønsted sites. The bands at 1630-20 cm^{-1} are omitted because both bases absorb in this region, whether adsorbed on Brønsted or

TABLE 1
ir Absorption Bands for Pyridine and 2,6 T Adsorbed on Acid Solids
in the 1400 cm^{-1} -1650 cm^{-1} Region^a

Pyridine ^{b,c}		2,6 T	
Coordinately bonded	PyH ⁺	Coordinately bonded	2,6 TH ⁺
1605-1630 (s)	~1620 (s)	1615-1630 (v.s.)	1615-1620 (v.s.)
~1580 (v)	~1640 (s)		1625-1640 (s)
~1495 (v)	1540-1550 ^d (v)	1505-1510 (m.s.)	1535-1545 (m.s.)
~1447-1465 (v)	~1490 (v)	1470-1485 (m.s.)	1470-1485 (m.s.)
		1425-1430 (s)	

^a Band intensities: v.s., very strong; s, strong; m.s., medium strong; v., variable.

^b Ref. 2.

^c Ref. 3.

^d This band cannot be present in coordinately bonded pyridine as it describes the N⁺-H bending motion contribution to the C-C ring vibration.

TABLE 2

Experiment	Degree of hydroxylation-OH	Brønsted 2, 6T 1545 cm ⁻¹	Lewis 2,6 T		Lewis pyridine 1455 cm ⁻¹
			1508 cm ⁻¹	1430 cm ⁻¹	
1 2,6 T first 2,6 T + pyridine	0.104	912	2,400	5,140	—
		935	2,174	4,528	2,010
2 Pyridine first Pyridine + 2,6 T	0.065	—	—	—	6,697
		257	527	1,604	4,797
3 2,6 T first 2,6 T + pyridine	0.248	1,111	2,685	5,432	—
		1,213	2,734	5,782	12,020
4 Pyridine first Pyridine + 2,6 T	0.112	—	—	—	11,992
		761	785	1,620	10,170

Note. Intensities of surface hydroxyl groups measured in absorbance units taken directly from the spectrometer chart. All data are normalized for a 20-mg sample.

Lewis acid sites. The bands at 1495 cm⁻¹ (pyridine) and 1475 cm⁻¹ (2,6 T) are similarly omitted from the table because of their mutual interference.

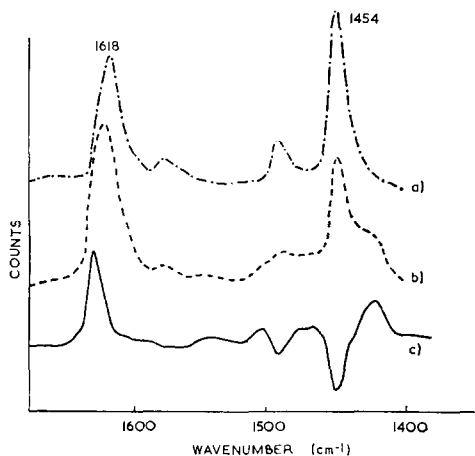


Fig. 3. Adsorption of 2,6 T on pyridine-treated γ -Al₂O₃ showing displacement of coordinately bonded pyridine. (a) Irreversibly adsorbed pyridine at 50°C. (b) Irreversibly adsorbed 2,6 T at 50°C on the pyridine-treated surface of γ -Al₂O₃ shown in spectrum (a). (a) and (b) have the background γ -Al₂O₃ spectrum subtracted. (c) Subtraction of (a) from (b) showing negative absorption bands for displaced pyridine.

Displacement of Pyridine

Figure 3 shows clearly the displacement of coordinately bound pyridine, as represented by the reduction of the 1495 and 1455 cm⁻¹ bands, on addition of 2,6 T. Table 2 shows that the amount of Lewis-bound pyridine displaced, as measured by the counts at 1455 cm⁻¹, is approximately constant at 1800, for both levels of hydroxylation.

Effect of Hydroxylation on Pyridine Adsorption

Figure 4 shows the effect of degree of hydroxylation on the amount of pyridine adsorbed when it is adsorbed first. Clearly more pyridine is adsorbed on the alumina sample with the greater hydroxyl population which is shown quantitatively in Table 2. The counts for the 1455 cm⁻¹ band correlate with the component of the hydroxyl band structure at 3690 cm⁻¹ which is selectively removed on adsorption of pyridine.

The effect of degree of hydroxylation on the amount of pyridine adsorbed, after

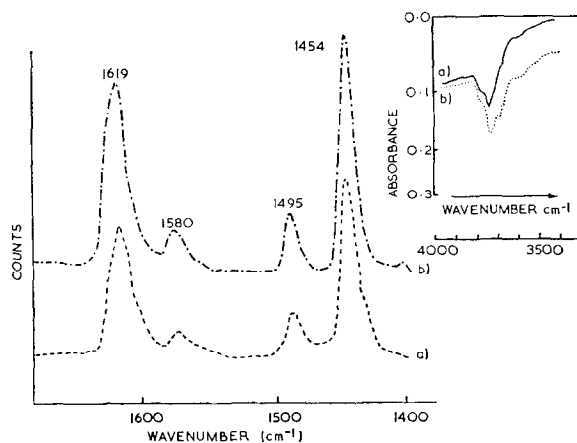


FIG. 4. Dependence of pyridine coverage on degree of surface hydroxylation of γ - Al_2O_3 . (a) and (b) show the irreversible adsorption of pyridine at 50° with background spectrum subtracted. Insert: (a) and (b) show the corresponding extents of surface hydroxylation prior to pyridine adsorption.

2,6 T has been adsorbed first (Fig. 5), follows the same pattern as in Experiments 2 and 4. Figure 5 also shows that the site on which 2,6 T adsorbs is independent of the hydroxyl population.

Coverage by the Bases

Five-tenths Torr of the two bases were separately adsorbed on samples of the

000-3P alumina, each pretreated for 1 hr at 350°C ; 7.8×10^{13} molecules of pyridine per cm^2 and 2.7×10^{13} molecules of 2,6 T per cm^2 were adsorbed on the alumina. Taking the molecular areas of pyridine and 2,6 T as 14.8 \AA^2 and 72.4 \AA^2 , respectively, the coverages for the bases are 11.8 and 19.9%.

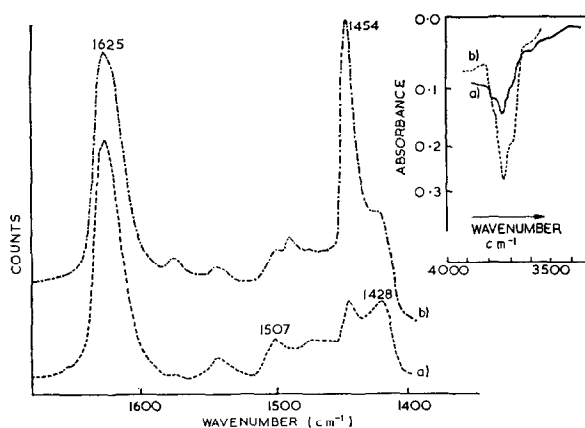


FIG. 5. Spectra showing the relative amounts of 2,6 T irreversibly adsorbed at 50°C followed by adsorption of pyridine on γ - Al_2O_3 with varying degrees of surface hydroxylation. (a) and (b) Pyridine adsorbed in the presence of irreversibly adsorbed 2,6 T with background spectrum subtracted. Insert: (a) and (b) show the corresponding surface hydroxylation prior to 2,6 T adsorption. These spectra show again the marked increase in pyridine adsorption with increasing surface hydroxylation.

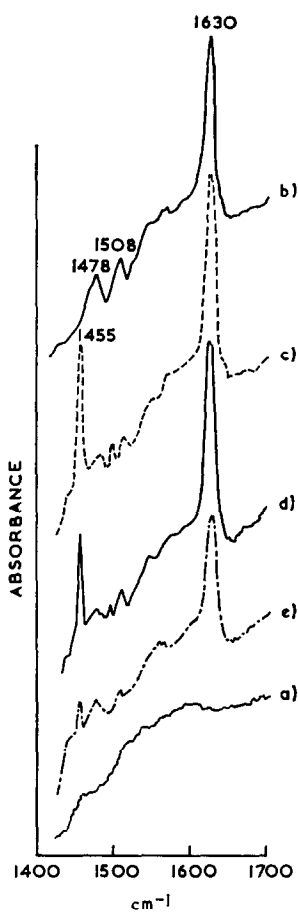


Fig. 6. Adsorption of 2,6 T and pyridine on CK 300. (a) Background spectrum after outgassing at 500°C. (b) Exposed to 0.5 Torr 2,6 T at 100°C and then outgassed at 250°C. (c) Exposed to 0.5 Torr pyridine at 100°C and then outgassed at 250°C. (d) Further outgassed at 250°C for 16 hr. (e) Outgassed at 450°C for 2 hr.

The Relative Strength of the Adsorption of the Bases

The adsorption of 2,6 T on another alumina (CK 300), pretreated under more severe conditions (500°C), was undertaken to widen the scope of these observations. Figure 6 shows the spectra of 2,6 T adsorbed on CK 300 with subsequent adsorption of pyridine and thermal treatment. As the temperature was raised from 250 to 450°C, the intensity of the band due to adsorbed pyridine (1455 cm^{-1}) was

reduced markedly while the 2,6 T band (1508 cm^{-1}) was only slightly reduced.

Brønsted Acidity of Alumina

Clarification of the strength of the Brønsted acidity demonstrated by the 1545 cm^{-1} band on adsorption of 2,6 T was necessary because of the unexpected nature of this result. 2,6 DMP did not give a band in this region on adsorption on alumina, but did show a band at 1545 cm^{-1} in its anhydrous hydrochloride and when it was adsorbed on hydrogen type Y zeolite. This band was not apparent in the solution spectra of 2,6 DMP hydrochloride either in ethylene dichloride or chloroform, whereas the 2,6 T hydrochloride clearly showed a band at 1535 cm^{-1} .

DISCUSSION

Band Assignment

The nature of the coordinatively bound 2,6 T will be discussed in more detail, but the assignment of the bands at 1508, 1475, and 1430 cm^{-1} to such a species is not in doubt. Why 2,6 T demonstrates Brønsted acidity and 2,6 DMP does not warrants further consideration. Examination of the pK_a values for 2,6 DMP and 2,6 T (11) shows the former to be the stronger base even allowing for the difficulty of solvating the protonated 2,6 T. On these grounds one would expect the 2,6 DMP to adsorb with equal facility on the weak Brønsted sites on alumina. The presence of such sites had already been demonstrated (6) by the formation of the ammonium ion on the surface of alumina dehydrated below 500°C. Jacobs and Heylen (9) were unable to detect a band at 1545 cm^{-1} for protonated 2,6 DMP but the authors have observed such a band for its anhydrous hydrochloride and 2,6 DMP adsorbed on the hydrogen form of type Y-zeolite. The absence of the 1545 cm^{-1} band in the solution spectra

of 2,6 DMP hydrochloride suggests a wide variation in its intensity in different environments, thus offering an explanation for the failure to observe it in the spectrum of the base adsorbed on alumina.

Steric Constraints Involved in the Adsorption of 2,6 T

The displacement of pyridine from Lewis acid sites by the highly hindered 2,6 T must lead to reconsideration of the accepted models for these sites. The experiments with CK 300 suggest that the sites on which 2,6 T adsorbs are among the strongest acid sites, in that this base is not substantially desorbed even at 400°C, whereas the majority of the coadsorbed pyridine is desorbed readily at 250°C. Figure 7 shows a scale diagram of 2,6 T adsorbed onto a model of a close packed alumina surface with the plane of the ring perpendicular to the surface and taking an appropriate Al-N bond length of 2.0 Å (12). The radii defined by the C-H bond length for the methyl groups of the tertiary butyl groups clearly indicate that these hydrogens would interfere with the surface if the nitrogen of the base was bonded to exposed aluminum ions. The 2,6 T is equally hindered in the plane of the aromatic ring thus eliminating the

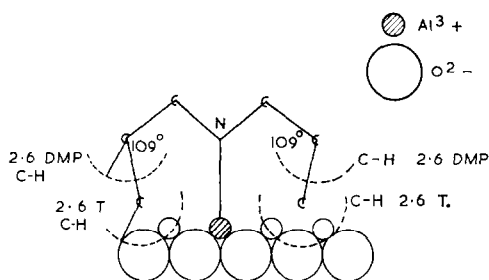


Fig. 7. Steric limitations in the bonding of 2,6 DMP and 2,6 T on exposed aluminum ion sites. The dotted lines represent the covalent radii of the hydrogens of the $-\text{CH}_3$ groups taking the C-H bond length as 1.10 Å, ionic radii of $\text{O}^{2-} = 1.32$ Å and $\text{Al}^{3+} = 0.51$ Å. Al-N bond length = 2.0 Å.

possibility of the base lying parallel to the surface. This leads to the conclusion that the sites which adsorb 2,6 T do not involve exposed aluminium ions in a close-packed face of alumina and further the displacement of pyridine by 2,6 T indicates that these sites adsorb pyridine.

Effect of Heat Treatment on Acid Sites

Experimentally it was found that although standard heat treatments were used as described, considerable variation in the degree of hydroxylation of the surface occurred as shown by the band intensities in their spectra. This is thought to be due to varying rates of water removal from pressed disks of different weights which were used in the experiments.

Independence of the amount of 2,6 T adsorbed on protonic sites over the limited range of hydroxylation suggests that only a small minority of the hydroxyls on the surface are involved. Similarly the degree of hydroxylation does not appear to affect the amount of coordinately adsorbed 2,6 T and implies that the sites concerned do not take part in an adsorption-desorption equilibrium with water.

The number of sites which adsorb only pyridine, i.e., those sites on which pyridine adsorb after 2,6 T has been preadsorbed (Table 2), increases with hydroxyl concentration. The correlation of these sites with the selective removal of the 3690 cm^{-1} band (Fig. 4) approximately follows the relationship

$$[\text{Pyridine}]_{1455\text{ cm}^{-1}} \propto [\text{OH loss}]_{3690\text{ cm}^{-1}}^2$$

This interaction is possibly associated with hydrogen-bonding of the ortho hydrogens of the coordinately bound pyridine to a hydroxyl adjacent to the Lewis acid site. On the basis of this limited evidence, one possible model for this "pyridine-only" site is shown in Fig. 8, where one hydroxyl holds another in a favorable position to hydrogen-bond to an ortho hydrogen of the coordinately held pyri-

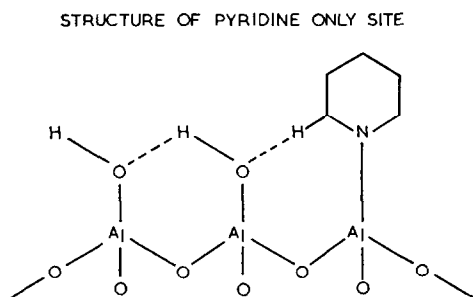


FIG. 8. A proposed structure for the "pyridine-only" site showing the association of the classical Lewis acid site with the surface hydroxyl groups.

dine. The ease with which these sites are lost on more prolonged heating at 350°C adds weight to the proposition that the two hydroxyl groups are juxtaposed.

Competition of 2,6 T and Pyridine

Further consideration of Table 2 leads to the proposition of a fourth site, in addition to the one protonic and two coordinate sites already described. The greater adsorption of 2,6 T when it is added first and the reduction in the amount of pyridine adsorbed if it is added second instead of first, suggests a site which irreversibly adsorbs whichever base is added first. An alternative explanation is that the pyridine adsorbed on the "pyridine-only" sites sterically hinders the sites on which 2,6 T would have adsorbed if unimpeded. Evidence against this latter explanation is the insignificance of the change in 2,6 T adsorbed on the less dehydroxylated samples which have the greater number of "pyridine-only" sites. Extra weight is added to this argument by the relatively low coverages of the bases adsorbed under these conditions.

Nature of the Strong Lewis Acid Sites

The series of competition experiments had demonstrated the presence of two different coordinating sites, both of which adsorb 2,6 T as well as pyridine. The steric implications of this phenomenon

have already been discussed and the possibility of coordination of 2,6 T through an "exposed" aluminum ion has been discounted. This leaves only one other possibility, namely that the coordination is through oxygen, either as an oxygen anion or a hydroxyl group. The independence of the amount of 2,6 T adsorbed with degree of hydroxylation suggests that coordination through a hydroxyl is unlikely. Consideration of the effect that an electron-deficient oxygen in a hydroxyl group would have on the acidity of its proton, virtually eliminates this possibility as there is no evidence of the strong Brønsted acid sites which such an arrangement would produce.

The concept of electron-deficient oxide ions or oxide defects on alumina (Fig. 9) is not entirely novel and has been invoked by Flockhart *et al.* (13) to explain the nature of electron donor and acceptor sites in radical cation formation. These electron-acceptor sites are, however, far less numerous than the sites observed in the present work and are perhaps related to the "exposed" aluminium ions detected recently by Lunsford *et al.* (14). The number of these sites measured at $1.0 \times 10^{12}/\text{cm}^2$ by EPR is an order of magnitude smaller than the sites studied here. The concentration of isomerization sites measured by Lunsford *et al.* using H_2S

SURFACE OF ALUMINA DEHYDRATED ABOVE 500°C

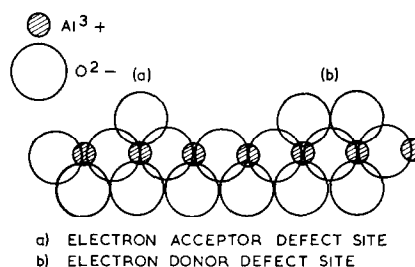


FIG. 9. A model of the close-packed alumina surface dehydrated above 500°C proposed by Flockhart *et al.* (13). (a) Electron acceptor sites. (b) Electron donor sites.

poisoning ($5 \times 10^{13}/\text{cm}^2$) is of the same order as the sites observed in this work. It is thus possible that a fraction of the strong Lewis acid sites are associated with aluminium ions accessible to nitric oxide, but the ir measurements show that pyridine and substituted pyridines are bonded to electron-deficient oxygen ions on these sites.

CONCLUSIONS

Four types of acid site have been identified on alumina, three coordinating sites and one protonic site, which though too weak to be detected by pyridine adsorption, reacts with 2,6 ditertiarybutyl pyridine. Two of the three coordinating sites interact through oxygen rather than aluminium and are differentiated by 2,6 T being unable to displace pyridine from one of them. The third apparently weaker coordinating site reacts with pyridine only and is closely associated with one or more hydroxyl groups.

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