

An Infrared Study of Pyridine Adsorbed on Acidic Solids. Characterization of Surface Acidity

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The infrared spectrum in the 1400 to 1700 cm^{-1} region has been determined for pyridine adsorbed on acidic solids. The spectrum of pyridine coordinately bonded to the surface is markedly different from that of the pyridinium ion. This permits the differentiation of acid type on the surface of acidic solids. From the frequency shift of one of the bands of coordinately bonded pyridine over that found in the liquid phase, and from the relative retention of the band upon evacuation and heating, a very rough estimate of the strength of surface Lewis sites can be inferred.

It is shown that a silica surface hydrogen bonds pyridine only. Alumina has considerable strong Lewis acidity but no proton acidity while a cracking catalyst has both. The effect on the acidity of sodium poisoning a cracking catalyst is discussed.

INTRODUCTION

The nature of the acidity of various catalysts and catalyst supports has been a matter of controversy for many years. A variety of techniques has been used to measure acidity including the use of indicators (1), titration with bases using indicators (2), measurement of the quantity of chemisorbed ammonia at various temperatures (3, 4), the use of dealkylation rates (5), the use of isomerization and dehydration rates (22), and the determination of the IR spectrum of chemisorbed ammonia (6, 7). The application of many of these techniques has given conflicting and widely differing results on the same materials. Moreover, none of the methods except the last one distinguishes between protonic acidity (Bronsted) and aprotic acidity of the Lewis type. Some of the procedures also suffer from other disadvantages such as diffusion limitations and/or extraneous physical adsorption.

The publications describing the IR spectrum of chemisorbed ammonia were preliminary in nature. Also, the ammonia band

that was used to determine the coordinately bonded ammonia was found to be subject to some interference. Moreover, ammonia is such a strong base ($\text{p}K_b \sim 5$) that it will react with extremely weak acid sites.

As a means of learning more about the nature of surface acidity, a brief study was made of the infrared spectrum of pyridine chemisorbed on various solids. The amount of pyridine adsorbed on acidic solids at high temperatures has already been used as a tool to measure acidity (8). While pyridine is also a relatively strong base, it is significantly weaker than ammonia ($\text{p}K_b$ pyridine ~ 9 ; $\text{p}K_b$ ammonia ~ 5), and thus will not react with some of the weaker sites that would react with ammonia. An indication might thus be obtained of the strength of the protonic sites on some weakly acidic solids. The use of much weaker bases would be helpful to further delineate acid strength.

Since one of the objectives of this study was to differentiate Lewis and Bronsted sites, the recognition of the possible formation of pyridinium ion (PyH^+) was of interest. The obvious way to do this would be to observe the band for the $\overset{+}{\text{N}}\text{—H}$ stretching vibration. However, this band is considerably smeared and its frequency lowered by hydrogen

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bonding (9); in solid pyridinium chloride, this vibration results in a very broad structureless band at approximately 2450 cm^{-1} (10). Because of this, and the fact that the hydroxyl groups of the acidic solids of interest readily form strong hydrogen bonds, this band could not be observed on any of the materials reported here.

It has been found that considerable information can be obtained about the acidity of various solids by studying changes in the "ring" vibrations of pyridine and other bands in the region of 1700 cm^{-1} to 1400 cm^{-1} . This paper describes the results of a preliminary study of the spectrum of pyridine in this spectral region on several catalytic solids. While this study is not extensive, it indicates the possibilities of this technique in studying changes in surface acidity of solids.

EXPERIMENTAL

Cell. The cell used for the work is shown in Fig. 1. The sample in the form of a thin

Dow Corning Hi-Vac stopcock grease has been found satisfactory to seal the standard taper joint. Heating of the sample was done externally by a heating coil over the upper portion of the arm. The vacuum system was conventional and was capable of evacuating the cell to pressure in the 10^{-6} mm Hg range.

Materials. The pyridine used was a heart cut of reagent grade material redistilled from sodium hydroxide.

The silica was Cab-O-Sil from G. L. Cabot Company, with a typical surface area of about $200\text{ m}^2/\text{g}$. The alumina was an eta alumina prepared by slowly calcining to 500°C in air a commercial Bayerite obtained from Morton Chemical Co. Its surface area was approximately $250\text{ m}^2/\text{g}$. Analytical data supplied by the manufacturer indicated the following level of impurities: $\text{SiO}_2 < 0.005\%$; $\text{TiO}_2 < 0.002$; $\text{FeO}_3 < 0.001$; $\text{Na}_2\text{O} < 0.001$. A commercial Houdry M-46 cracking catalyst was used with a typical surface area around $325\text{ m}^2/\text{g}$.

Sample preparation. Samples were pressed

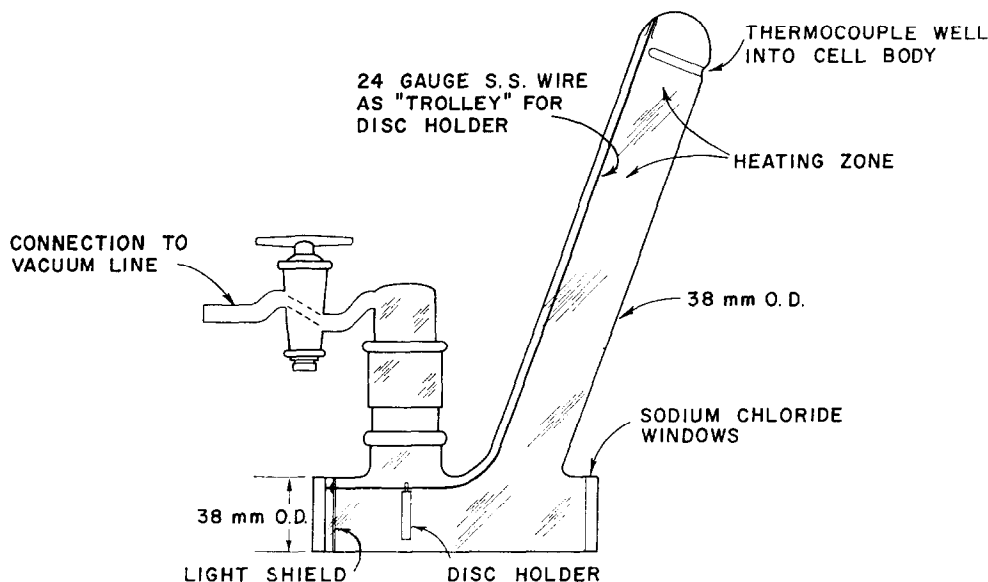


FIG. 1. Design of infrared cell.

self-supporting wafer was mounted in the stainless steel holder and placed in the cell over the trolley wire. The sample could thus be slid back and forth along the wire either into the heating arm for treatment, or into proper position to record the spectrum.

into self-supporting wafers of 1 inch diameter using a pressure of approximately 40,000 psi. The optical thickness was approximately $25\text{ mg}/\text{cm}^2$. After pressing, the discs were mounted in the cell and dehydration was begun. After dehydration, a background

spectrum was usually recorded, then pyridine was admitted. Generally, approximately 0.05 mole (excess) of pyridine was initially admitted, then the spectrum was recorded after evacuation at various elevated temperatures. All spectra were recorded after cooling the sample to room temperature.

A sodium-poisoned cracking catalyst was prepared by grinding some M-46 catalyst to a fine powder, then slurring in a solution containing sufficient sodium acetate to give a final sodium content of the catalyst of 0.8 meq Na/g. After standing for 48 hr with occasional stirring, the catalyst was dried under an infrared heat lamp and calcined in air at 500°C for 16 hr.

Spectroscopic technique. Spectra were recorded on a Perkin-Elmer Model 221 double-beam prism-grating spectrophotometer. The instrument was continually flushed with dry air to remove H₂O and CO₂. For some of the samples, it was necessary to attenuate the reference beam with screens and to widen the slit to compensate for loss of energy by scattering.

RESULTS AND DISCUSSION

Assignment of Spectrum of Pyridinium Ion and Coordinately Bonded Pyridine

While several workers have discussed the assignments of the infrared spectrum of pyridine (11, 12, 13), little was known about changes in the spectrum when pyridine was either coordinately bonded or in the form of the pyridinium ion. Because the pyridinium ion has the extra hydrogen atom not present in pyridine, the species should have three additional fundamentals in the spectrum.

One of these, the $\overset{+}{\text{N}}\text{—H}$ stretching vibration is so broad if it is hydrogen-bonded that it cannot be observed, as mentioned earlier. (A dehydrated silica with added HCl does give the band, but it is very broad and difficult to observe.) Since other significant changes might be found between pyridine and pyridinium ion in the so called "ring frequency" region this was examined in some detail. Figure 2 gives three typical spectra which do indeed show that the pyridinium ion gives a band at approximately 1540 which is not present in either pyridine or

coordinately bonded pyridine (Py · BH₃)*. Also from Fig. 2, it can be seen that the pyridinium ion does not have a band in the 1440–1465 cm⁻¹ region but both coordinately bonded pyridine and hydrogen-bonded pyridine do. From additional runs with other complexes (Cu and Sn chlorides) and from the work of Terenin (15) (pyridine complexes of AlCl₃, AlBr₃, SnCl₄), it is clear that coordinately bonded pyridine complexes have a band in the range 1440–1465 cm⁻¹ and the frequency increase of the band appears to be related to the stability of the complex. Additional evidence for this relation comes from a rough correlation between ease of pumping off the pyridine and the frequency of the band, as will be described below.

It is clear from the present work and other published work (15–17) that the 1583 cm⁻¹ band also shifts markedly when pyridine is coordinately bonded. Barrow (17) has studied the shift of this band with hydrogen bonding and has indicated that the larger shifts indicate increasing hydrogen bond strength. This band would also be useful as an indication of aprotic (Lewis) acidity but it is interfered with by water vapor when present, and the 1620 cm⁻¹ vibration of pyridinium ion.

Recently, work has appeared (16) which confirms the differences we found between coordinately bonded pyridine and pyridinium ion and assigns the 1540 cm⁻¹ pyridinium band, on the basis of some deuteration experiments, to a combination mode which involves the $\overset{+}{\text{N}}\text{—H}$ deformation.

This means that the $\overset{+}{\text{N}}\text{—H}$ configuration has to be present in order that the infrared band be found. This band could not be obtained therefore with a very strong Lewis acid.

It is thus possible to use the band at 1540 cm⁻¹ along with the band near 1640 and the very intense band at 1485 cm⁻¹ to indicate proton acidity, while a band in the 1440–1465 cm⁻¹ region indicates aprotic acidity, with a rough indication of the strength of the acidity being given by the frequency of the band. These assignments are given in Table 1.

* Compound obtained courtesy Callery Chemical Co., Pittsburgh, Pa.

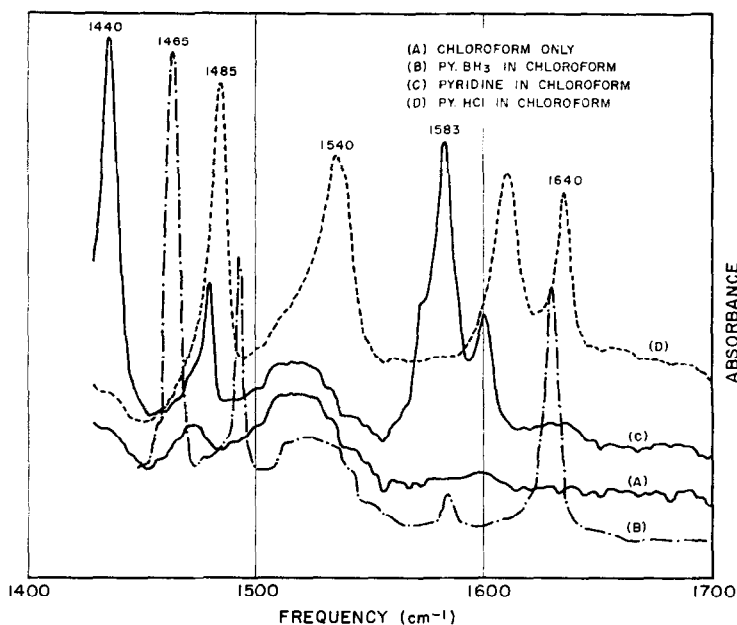


FIG. 2. The infrared spectra of pyridine, coordinately bonded pyridine, and the pyridinium ion.

Pyridine on Silica

After dehydrating a disc of silica at 400°C for 3 hr then adding pyridine and pumping off, the spectrum shown in Fig. 3 is obtained. The two bands at 1447 cm^{-1} and 1599 cm^{-1} show hydrogen-bonded pyridine only. There is no evidence for a band at 1540 cm^{-1} , which indicates proton acidity, and the shift of the 1440 cm^{-1} band is not large enough

to indicate Lewis acidity. Moreover, the pyridine can be pumped off at 150°C, indicating that the pyridine is relatively weakly held to the surface sites. The frequency shift is in the range to be expected for pyridine hydrogen-bonded to surface OH groups. Roev also reported no proton acidity on silica by examination of the infrared spectrum of adsorbed ammonia (18), and

TABLE 1
INFRARED BANDS OF PYRIDINE ON ACID SOLIDS IN THE 1400–1700 cm^{-1} REGION^a

Hydrogen bonded pyridine	Coordinately bonded pyridine	Pyridinium ion
1440 ^{b,c} –1447 (v.s.)	1447 ^{b,c,d} –1460 (v.s.)	
1485–1490 (w)	1488–1503 (v)	1485–1500 (v.s.) 1540 ^e (s)
1580 ^{b,c} –1600 (s)	~1580 (v) 1600 ^{b,c} –1633 (s)	~1620 (s) ~1640 (s)

^a Band intensities: v.s.—very strong; s—strong; m—medium; w—weak; v—variable.

^b The split between hydrogen-bonded and coordinately bonded pyridine (Lewis base) is not well defined by band frequency alone. Other conditions need be used where possible, such as ease of pumping off, etc.

^c Frequency appears to increase with increasing bond strength.

^d This band is not present in the pyridinium ion spectrum. This, with auxiliary bands listed, can be used to determine Lewis acidity.

^e This band cannot be present in coordinately bonded pyridine (Lewis base) since the N⁺—H bending motion is involved in the vibration. Thus a proton has to actually transfer to the nitrogen in order for this band to appear. This band together with auxiliary bands listed, is used to characterize proton sites.

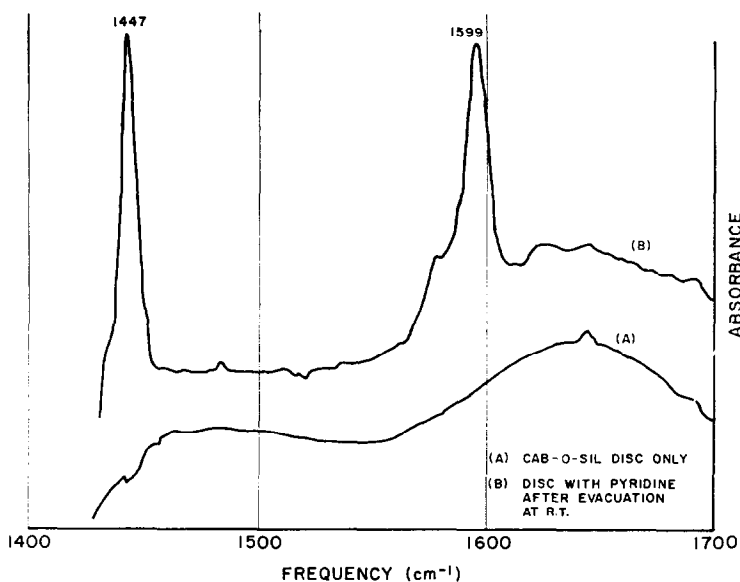


FIG. 3. The infrared spectrum of pyridine adsorbed on Cab-O-Sil silica disc. (A) Cab-O-Sil after evacuation at 400°C; (B) after exposure to pyridine then evacuation at room temperature.

Eischens (6) reported that silica physically adsorbs ammonia only.

Pyridine on Alumina

The type and strength of acidity on alumina has been a matter of controversy for some time. Hirschler *et al.* have reported that Alcoa F-10 alumina has stronger acidity than a cracking catalyst (20) even in the absence of chloride (21). They used an amine titration and various Hammett indicators to get an acidity distribution. From some of their data, they inferred that the acidity on alumina is different in kind from that on a cracking catalyst even though both respond to Hammett indicators. Pines *et al.* (22), using different indicators, concluded that aluminas had Lewis acidity.

Eischens found spectral bands for ammonium ion (7) but failed to find bands for ammonia which would be indicative of strong Lewis-type bonding (23). Our experiments using the spectral bands of adsorbed pyridine do indeed indicate that the strong acid sites on alumina are of the Lewis acid type.

The spectrum of pyridine adsorbed on a dehydrated eta alumina is shown in Fig. 4. Upon recording the spectra after evacuation at successively higher temperatures, we

observe that the band at 1450 cm^{-1} gradually narrows, its intensity decreases, and an increase in the frequency of the maximum occurs. This obviously indicates that the more weakly surface bonded pyridine has the lower frequency. After evacuation at 150°C, a doublet can be observed, with the lower frequency peak disappearing first with evacuation at increasingly elevated temperatures. The data suggest that there are at least two groups of Lewis sites on the surface of the dehydrated alumina differing in acid strength. The frequency of this peak after the high-temperature evacuation is similar to that reported by Terenin (15) for complexes of pyridine with typical Lewis acids such as AlCl_3 , AlBr_3 , etc. The retention of pyridine after evacuation at high temperatures, as evidenced by the 1459 cm^{-1} band, the shift in frequency of this band, as well as the large frequency shift of the 1583 cm^{-1} band (to 1632 cm^{-1}), is indicative that the dehydrated alumina is a strong Lewis acid. The band at 1600 cm^{-1} in the room temperature spectrum represents hydrogen-bonded pyridine and the band at 1583 cm^{-1} represents physically adsorbed pyridine. These frequencies are in substantial agreement with the literature values (17, 24).

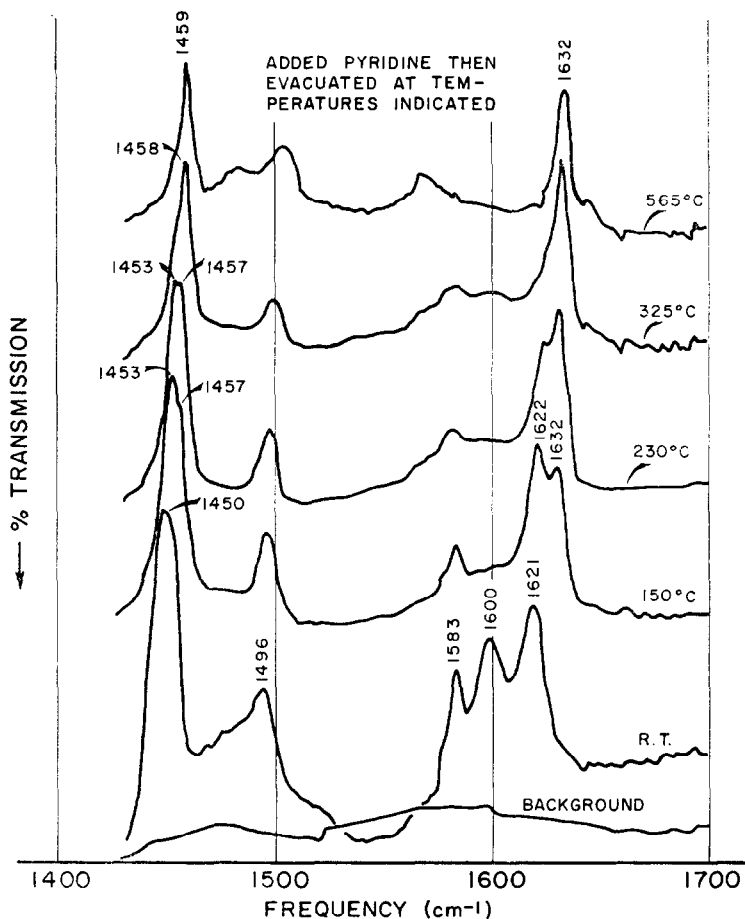


FIG. 4. The infrared spectrum of pyridine on eta alumina. Background spectrum was obtained after evacuating sample at 450° for 3 hr. After pyridine addition, spectra were recorded after evacuation for 3 hr at the temperature indicated.

Both bands disappear after evacuation at 150°C as would be expected. The small band at 1580 cm⁻¹ left at higher temperatures arises from coordinately bonded pyridine. (See curve B of Fig. 2, where a small band is found at ~1585 in the Py · BH₃ spectrum.) Thus all spectral bands in the 1700–1400 cm⁻¹ region can be assigned.

No evidence is found for a band at 1540 cm⁻¹ on the alumina indicating that there are no Bronsted sites on the surface strong enough to react with pyridine. The addition of excess water vapor (approximately 0.05 mole) to a disc containing pyridine also does not give a spectrum which shows the presence of significant amounts of the pyridinium ion (1540 cm⁻¹ band). We conclude therefore

that any protons present on the alumina are too weak to react with pyridine. Because Eischens reports that he found ammonium ion on a hydrated alumina (7), the strength of protons on an alumina must be very weakly acid to react with ammonia ($K_b = 10^{-5}$) and not react with pyridine ($K_b = 10^{-9}$). An alternative explanation for this observation (i.e., finding an infrared band for ammonium ion but not pyridinium ion on hydrated alumina) could involve an unfavorable ratio of absorptivities (extinction coefficients) for these bands when the ions are on the alumina. Since the ratio of absorptivities in solution (ammonium ion/pyridinium ion) is about 1.7, the intensity ratio on alumina is 10 or greater, and the

vibrational modes are somewhat similar, this does not seem likely. However, the possibility cannot be completely ruled out.

Pyridine on Cracking Catalysts

Eischens (6) has already shown that protonic acidity exists on partially dehydrated cracking catalysts by observing the infrared spectrum of ammonium ion. We find both pyridinium ion as well as strongly coordinately bonded pyridine on the surface of a moderately dehydrated M-46 cracking catalyst. Figure 5 shows the

spectrum shows changes which occur upon addition of 0.05 mole of water to the previous sample. The spectral changes indicate that considerable Bronsted acidity has been formed (increase in 1540 cm^{-1} band) with a concomitant decrease in Lewis acidity (decrease in 1450 cm^{-1} band). Eischens inferred from his data that interconversion of Lewis and Bronsted acid sites occurred but was unable to observe it clearly because the ammonia band he used was partially obscured by an infrared band of water. Tramhouze (25) observed a reversible interchange

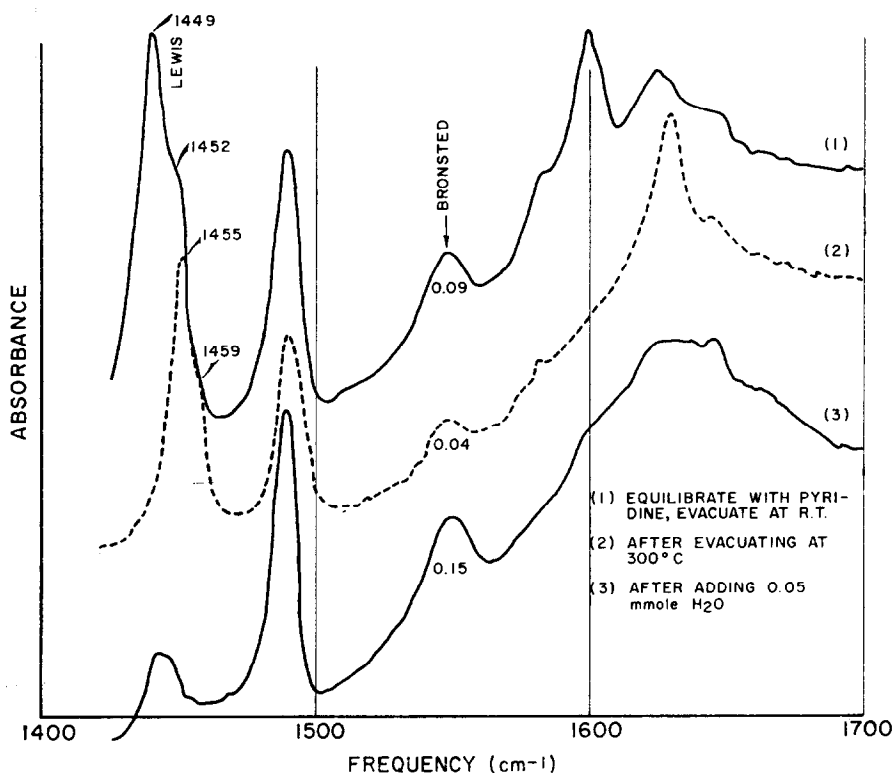


FIG. 5. The infrared spectrum of pyridine on an M-46 cracking catalyst. No background spectrum recorded, but disc evacuated for 3 hr at approximately 350°C before pyridine added.

spectra. After addition of pyridine to a disc previously dehydrated at 350°C , the presence of the band at 1540 cm^{-1} shows clearly the presence of the pyridinium ion. After evacuating at 300°C , some pyridinium ion is still left but the spectrum now shows clearly the presence of Lewis acidity on the cracking catalyst which appears to be quite strong ($1455\text{--}1459\text{ cm}^{-1}$ bands). The third

of the two types of acid sites using titration techniques. The present data confirm such an interconversion.

The effect of the presence of alkali ions on the spectrum of chemisorbed pyridine is also of interest. A number of workers (26, 27) have demonstrated that addition of alkali ions to cracking catalysts destroys or reduces its activity. The presence of alkali

ions is shown here to affect both types of acid sites.

After evacuation of an M-46 sodium-poisoned cracking catalyst disc at approximately 400°C for 2 hr in the cell, adding pyridine, then pumping off at room temperature, the spectrum shows that both the Lewis and Bronsted sites have been affected. (See Fig. 6, spectrum 1.) The intensity of

ever, a marked decrease in number of sites over the unpoisoned catalyst is obvious. The spectral data show that sodium poisons both types of acid sites on the catalyst surface.

Because of the excess of the alkali metal ion (0.8 meq/g) over the usual amount of acidity which these catalysts have (~ 0.3 meq/g), it would be expected that no proton acidity should be left on the treated catalyst.

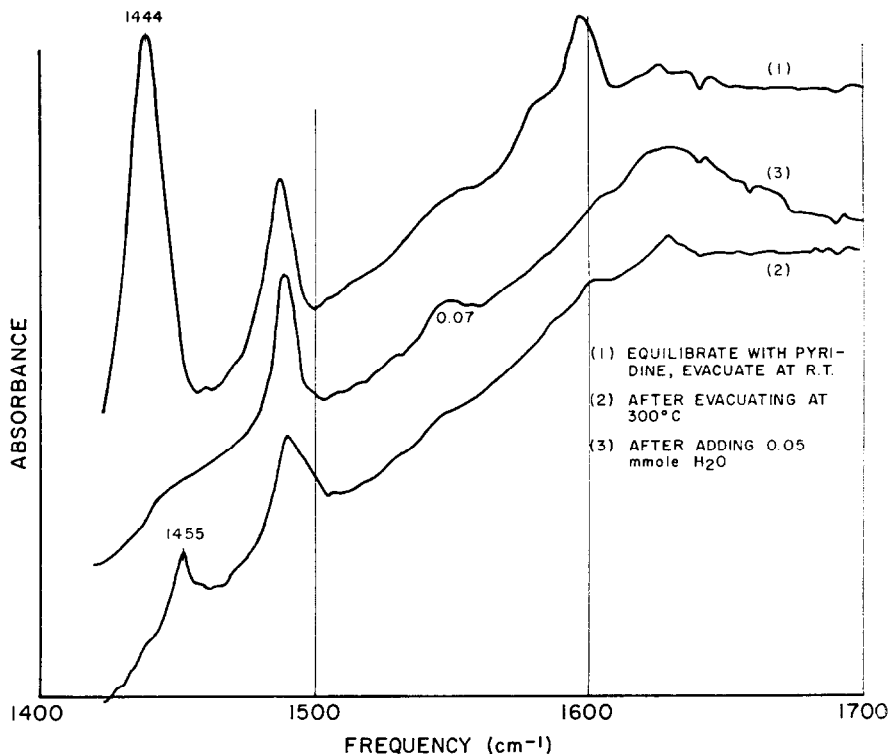


Fig. 6. The infrared spectrum of pyridine on a sodium-poisoned M-46 cracking catalyst. No background spectrum was recorded but sample evacuated for 2 hr at approximately 400°C before pyridine added.

the pyridinium band at 1540 cm^{-1} has markedly decreased, while the strength of the Lewis sites has been decreased as evidenced by the occurrence of the band at lower frequency (1444 cm^{-1} vs 1447 cm^{-1} for the non-sodium-treated). After evacuation at 300°C (spectrum 2), the intensity of the 1455 cm^{-1} band is much smaller than for the unpoisoned catalyst which again indicates fewer strong sites. Addition of 0.05 mole of water shows that some proton sites still exist on the catalyst (1540 cm^{-1}). How-

ever, Benesi (1) found that treatment of a cracking catalyst with excess sodium ion, then calcining, gave a catalyst which still showed acidity. He postulated that the large hydrated sodium ion originally covered up several sites which again became exposed and active after calcination and removal of the water of hydration. Further study of this point should be made.

The use of the infrared technique and particularly the use of the spectrum of pyridine thus appears to be a useful means

for delineating protonic and aprotonic acidity on surfaces and to find what effect various treatments have on the surface acidity.

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