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A Spectrophotometric Study of the Acidity of Some Solid Acids

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Weakly basic Hammett and H_R indicators were used to characterize the strongest sites of some solid acids. A spectrophotometric method was devised because it was demonstrated that conclusions reached by observing color changes can be very misleading. The method provided a means to measure the amounts of indicator adsorbed and the rates and efficiency of the adsorption. The data suggested that adsorption equilibrium with all of the surface cannot be achieved and that in some cases the pore mouths of zeolites become blocked by irreversibly adsorbed molecules. Nevertheless the results obtained ranked the catalysts correctly in order of increasing acidity as judged by catalytic measurements. The strongest acid found was an H-mordenite showing sites with $H_o < -12.4$. Some of the problems encountered in making meaningful acidity measurements and in their interpretation are discussed. © 1990 Academic Press, Inc.

INTRODUCTION

Improved methods are needed for the assay of solid acids. The recent literature contains several references to superacid characteristics (*1–9*). Usually this has meant that a process known to occur in liquid superacids has been observed, e.g., the skeletal isomerization of paraffins at or near room temperature or evidence suggesting that stable carbenium ions have been formed on the catalyst surface. This leads naturally to the questions, "If we had a solid superacid, how would we recognize it?" and "Just how strong an acid is a particular zeolite relative to another or to some standard, e.g., magic acid?" Several attempts have been made to address these questions using Hammett indicators, but a number of problems exist which limit the validity of the results and these are addressed herein.

It is convenient to think of acidity in terms of its extensive and intensive properties. With zeolites, the former (the number of Brønsted sites per gram) is frequently taken as the lattice aluminum concentration. Moreover, in silica-rich materials, it has been assumed that the Brønsted sites all have the same strength because they are sufficiently remote from each other so that they do not interact. The intensive factor cannot be so simply defined. It must reflect the ease of proton transfer to a given base, and it must also take into account the stability of the protonated base on the surface (its lifetime). This may be a function of how well the excess negative charge left on the zeolite lattice can be delocalized. An analogous situation is to be found in solutions of oleum. The acidity of these solutions increases as SO_3 is added into 100% H_2SO_4, not by increasing the proton content but by increasing the size of the molecule. When a base is protonated the conjugate $HS_2O_7^{-1}$ is formed (rather than HSO_4^-). Thus, weaker bases can be protonated (BH^+) by oleum solutions than by H_2SO_4. Similar acidity enhancement can be found in Friedel-Crafts acids such as HCl-$AlCl_3$, HF-SbF_5, and magic acid ($HOSO_2F$–SbF_5). In all cases the acidity is enhanced as the size of the anion (the conjugate base in which the electron is delocalized) is increased. These ideas may be illustrated by considering the equilibrium

$$B + HA \overset{K_a}{\rightleftharpoons} BH^+ + A^-, \qquad (1)$$

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which is established when the rate of the forward reaction is equal to the rate of the reverse reaction. The former will depend on the intrinsic ease of proton donation by the acid HA to the base, whereas the latter will depend on the stability of A^- in its local environment. The more stable this ion the longer the lifetime of conjugate acid BH$^+$, and hence its propensity for undergoing secondary reactions. The steady-state concentration of BH$^+$ is thus a measure of the lifetime and this will be dependent on the stability of A^-, which is a property of the acid only.

Hammett indicators have been used for many years to assay the strength of various liquid and solid acids. This subject has been repeatedly reviewed (*10–15*) and need not be discussed in detail here. This is a thermodynamic approach based on the equilibrium

$$B + \mathrm{H}^+ \xrightleftharpoons{K_{BH^+}} B\mathrm{H}^+, \qquad (2)$$

which differs from (1) by the ionicity of the acid,

$$\mathrm{H}A \xrightleftharpoons{K_i} H^+ + A^-. \qquad (3)$$

Equation (2) does not consider the conjugate base of the acid explicitly, although this factor is critically important to the lifetime of the carbenium ion. On the other hand, the formalism of Eq. (2) leads to the definition of the well-known parameter H_0 on which so much literature is available, i.e.,

$$\begin{aligned} H_0 &= -\log a_{\mathrm{H}^+}(f_B/f_{B\mathrm{H}^+}) \\ &= \mathrm{p}K_{B\mathrm{H}^+} - \log(C_{B\mathrm{H}^+}/C_B). \qquad (4) \end{aligned}$$

This method has proved useful because the parameter H_0 is analogous to pH; it is a state function which can be numerically evaluated so that comparisons can be made among solid and liquid acid systems. We have adopted it herein because it can provide answers to the important questions posed above concerning the onset of superacidity, which is conventionally defined as any acid stronger than 100% H_2SO_4 or having an $H_0 < -12$ (*16*). For the present purposes we have adopted Walling's approach (*17*), modified by use of spectroscopic measurements to determine the weakest base which can be protonated to a significant extent by the solid acid. Also, p$K_{B\mathrm{H}^+}$ values derived from the more recent literature (*14, 16, 18*) have been employed to determine the H_0 values of the strongest sites. Thus, the ratio $C_{B\mathrm{H}^+}/C_B$ (Eq. (4)) was not measured, but BH$^+$ was definitely detected by spectrophotometric means. As noted earlier (*13, 19*), it is now shown that the detection of BH$^+$ by color change can lead to grave misinterpretation of the data, particularly if the peaks of both the neutral indicator and of its protonated form lie in the ultraviolet region of the spectrum.

EXPERIMENTAL

Catalysts and pretreatment. The catalysts studied and their physical properties are listed in Table 1, together with information concerning their origin. Unless stated otherwise, they were used as received following a standard pretreatment. In this the catalysts were calcined in a stream of dry O_2 as the temperature was raised from room temperature (at 5°/min.) to 500°C, where it was maintained for 12 hr. The flow rate was 60 ml/min. Following this treatment the cell was evacuated to 10^{-6} Torr over a period of 2 h before cooling to room temperature. BET surface areas are given for the amorphous silica–alumina catalysts and pore volumes for the zeolites (determined from the capillary condensation of N_2 at $P/P_0 = 0.5$). These latter values suggested that the pore systems were not seriously contaminated with extraneous material. The chemical compositions and Si/Al ratios obtained from chemical analysis may be compared with those obtained from ^{29}Si MASNMR, i.e., the lattice aluminum values. Higher values of the former indicate that extralattice alumina is present. This has been shown to profoundly affect the catalytic activity (*1a, 4a*) and presumably the acidity. Another anticipated limiting factor

TABLE 1

Summary of Properties of the Catalysts Used and Their Origin

Adsorbent	Si/Al chemical analysis	Si/Al framework[a]	Framework Al/g × 10^{-20}	Total Al/g × 10^{-20}	Surface area (m^3/g)	Pore volume (cm^3/g)	Source of parent material
Davisil 62 (silica gel)	—	—	—	—	340	1.2	W. R. Grace Co.
M-46 silica–alumina (12.5% Al_2O_3)	5.9	—	—	—	270	0.6	Houdry Co.
N-631-L silica–alumina (13% Al_2O_3)	5.7	—	—	—	500	0.6	Nikki Co.
LZ-Y82	2.9	5.2	15.8	28.3	—	0.32 (0.32)[b]	Linde Co.
LZ-210(12)	5.9	6.0	14.6	14.9	—	0.33 (0.32)[b]	Linde Co.
HY(8.1)[c]	8.1	13	6.9	11.0	—	0.3 (0.32)[b]	LZ-Y62 Linde
HM(7.3)[c]	7.3	11	7.9	11.9	—	0.20 (0.20)[b]	2900H Norton
LZ-M8	8.5	—	—	10.6	—	0.18 (0.20)[b]	Linde Co.
JRC-Z-HM(20)	10.0	—	—	9.2	—	0.14 (0.20)[b]	Jap. Standard
Beta	19.1	—	—	5.0	—	0.31 (0.20)[d]	PQ Corp.
H-ZSM-5(39.7)	34.7	35	2.8	2.8	— —	0.2 (0.18)[b]	Mobil Corp.

[a] Si/Al framework obtained from ^{29}Si MASNMR.

[b] Pore volumes calculated from structural data.

[c] The HY(8.1) and HM(7.3) were hydrothermally dealuminated; see Ref. (*5a*).

[d] Given in Ref. (*33*).

may be how readily the indicator molecule enters the pore system, i.e., its size and shape, and the possibility that it plugs the pore mouths by irreversible adsorption on the first sites it contacts.

Apparatus. For the optical measurements, thin wafers (7–10 mg/cm^2) were pressed; pressures of about 5000 psi were needed to obtain platelets having sufficient strength to withstand the subsequent treatment. These wafers were put into a quartz UV cell which was attached through a graded seal to the Pyrex system having the configuration shown in Fig. 1. This apparatus was attached to a conventional high-vacuum BET system for pretreatment of the self-supporting wafers and it was used for subsequent spectroscopic examination.

Procedures. Measured 4-cm^3 aliquots of the appropriate solvent were introduced into tubes fitted with break-off seals. The liquid was degassed at 78 K by use of a freeze–pump–thaw cycle before sealing under vacuum. These tubes formed Part A in the assembly shown in Fig. 1. After pretreatment of the catalyst wafer, the assembly was isolated under vacuum and removed from the rack. The break-off seal was then ruptured and the unsupported catalyst was submerged in 4 cm^3 of pure solvent in the quartz optical cell. Now, with the catalyst protected from the atmosphere

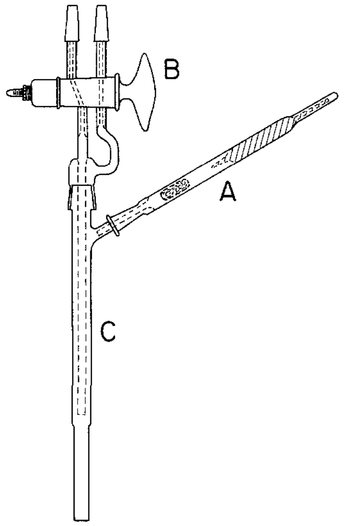

FIG. 1. Apparatus for spectral measurements of adsorbed molecules. (A) Pyrex tube with solvent and break-off seal; (B) stopcock assembly with quartz tube for flowing gas; (C) quartz tube with UV cell (1 × 1 cm).

by solvent, Parts A and B were removed from the assembly and the joints of C were wiped clean of stopcock grease and recapped. The cell could be opened as needed to add an additional 1-cm^3 aliquot of a solution of the indicator in the same solvent. The concentrations of the final solutions could be adjusted to accommodate differences in extinction coefficients, molecular size, and adsorption capacity of the adsorbent. Thus, about 1 μmol of triphenylmethanol, 0.03 μmol of benzylacetophenone, 4 μmol of 2,4,6-trimethylbenzyl alcohol, 0.07 μmol 4-nitrotoluene, 0.14 μmol 4-nitrofluorobenzene, and 0.07 μmol 2,4-dinitrotoluene were added to wafers weighing approximately 15 mg. Thus, between 1.2×10^{18} and 2×10^{20} molecules/g were available for adsorption, and more generally the amount added amounted to about 1% of the base-exchange capacity. These conditions were selected to probe the surface without masking of the protonated forms of the indicators by adsorption of excess neutral indicator. They copied the old convention of testing the acidity with insufficient indicator to disturb the existing H_0 (or pH). Note that all the indicators used have relatively high extinction coefficients (10^3 to 10^5 cm^2 mmol^{-1}) in both the neutral and the protonated forms.

The baseline spectrum was obtained by transmission of the beam through the wafer immersed in the solvent with the pure solvent in the reference beam (Fig. 2B). After adding the indicator solution to the sample cell, the spectrum was redetermined vs the pure solvent (Fig. 2A) at various times between 10 and 90 min. After recording each Spectrum A, the sample cell was rotated by 90° so that the amount of indicator left unadsorbed in the solution could be determined (Spectrum 2C). Thus the spectrum obtained from the *adsorbed* indicator could be obtained by subtraction of Spectrum B and Spectrum C from the corresponding Spectrum A using the computer attachment of the 8450A Hewlett–Packard diode ray spectrometer. (This instrument has good resolution up to absorbance values of about 3.7.) The difference spectrum obtained after 60 min from 4-nitrofluorobenzene adsorbed on HY(8.1) is shown in Fig. 3; this is

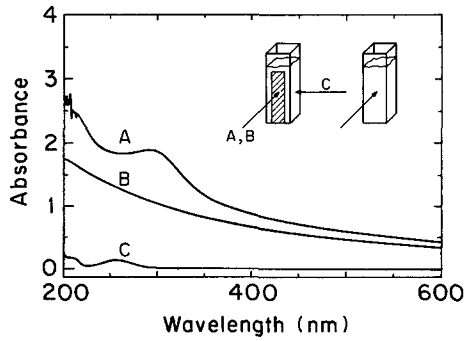

FIG. 2. Absorption spectra from 4-nitrofluorobenzene adsorbed on HY(8.1). (A) Spectrum with the beam through the catalyst and solution; (B) spectrum through the catalyst and the n-heptane solvent (before adding the indicator); (C) spectrum through the residual 4-nitrofluorobenzene solution (the cell was turned 90° immediately after recording A). The reference sample for Spectra A, B, and C was pure n-heptane.

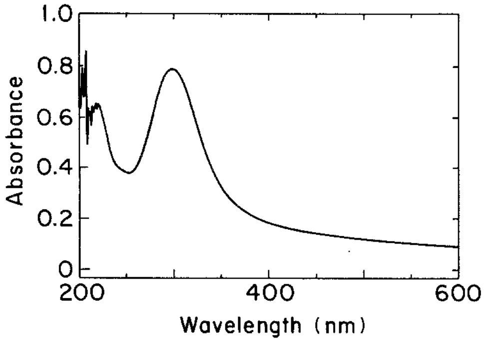

FIG. 3. Adsorption spectrum of the 4-nitrofluorobenzene indicator adsorbed on HY(8.1) after 60 min (obtained by subtraction of Spectra B and C from Spectrum A; Fig. 2).

the spectrum of the unprotonated form of the indicator and may be taken as typical of our results. Even though the peak is in the UV region, a yellow color was clearly evident on the platelet stemming from the tail into the visible region above 400 nm.

The spectra obtained in Mode C could be used to follow the disappearance of the indicator from the solution as it was adsorbed on the solid. Typical data are shown as Fig. 4 for 4-nitrofluorobenzene adsorbing on HY(8.1). Such data allowed adsorption rates to be estimated and these varied considerably with the structure of the zeolite and the extent to which the pore system may have been distorted or plugged.

Reagents and gases. The O_2 was Linde "Extra Dry" grade. The indicators were purchased from Aldrich Chemical Co. and used for the preparation of dilute solutions without further purification. The solvents were *n*-heptane (Mallincroft) and benzene (Aldrich); both were spectroscopic grade. To ensure removal of trace amounts of H_2O, the latter was treated over a relatively large amount of freshly activated (at 500°C) silica gel.

The acids and superacids used, 95% and fuming sulfuric (30% SO_3) and magic acid (SbF_5/HSO_3F = 1), were all Aldrich products and were used to produce reference spectra without further purification.

RESULTS

The positions of the peak maxima determined for the catalysts tested are recorded in Table 2 together with values obtained in neutral solution and in magic or sulfuric acid. These latter data are in good agreement with the literature values (*16, 18, 20*). Moreover, the peak positions of the protonated forms varied by no more than a few nanometers, regardless of whether the species was formed in magic acid, H_2SO_4, or on the surfaces of the various adsorbents. As reported previously (*13, 19, 20*), however, the peak positions of the spectra of the neutral forms were not constant; they shifted to longer wavelengths as the interaction between the substrate and the catalyst increased. As can be seen in Table 2, sometimes these shifts could be very large (up to 60 nm). This matter will be dealt with in more detail in a later paper.

The indicators used are listed in Table 2 in the order of their decreasing basicity; their pK_{BH+} values are given in the second row. Data for the Hammett indicators were taken from Refs. (*16, 18*). The H_R indicators were not protonated; they reacted forming H_2O and a carbenium ion; hence the formalism of Eq. (4) does not apply to them directly. For convenience of comparison, however, the equivalent pK_{BH+} values listed correspond to the concentrations and

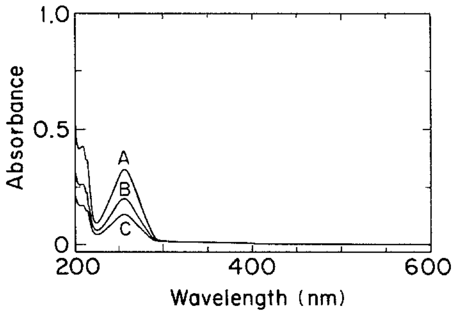

FIG. 4. Absorption spectra were taken from a 4-nitrofluorobenzene solution in *n*-heptane in contact with HY(8.1). A, B, and C correspond to 0, 60, and 90 min, respectively.

TABLE 2

Indicators Studied and Their Spectroscopic Peak Positions (nm)

Indicator[a]	Ph_3COH[b]	BzAP	TMBzOH[b]	4NT	4NFB	2-4DNT
pK_{BH+} −3.3	−3.3	−5.6	−8.7	−11.3	−12.4	−13.7
Neutral forms[c]	215	300	265	264	255	234
	260					
Acid forms[d]	410	415	470	377	360	339
	430					
Davisil 62	260	315	—[e]	285	274	265
M-46	410	395	—[e]	303	285	265
	430					
Nikki	410	400	—[e]	302	286	264
	430					
LZ-Y82	410	420	470	330	302	267
	430					
LZ-210(12)	410	415	470	317	299	266
	430					
HY(8.1)	410	415	470	318	299	266
	430					
LZ-M8	410	420	470	318	300	268
	430			375	360	
JRC-Z-HM(20)	410	420	470	318	300	268
	430			375	360	
Beta	410	415	470	318	299	266
	430					

[a] Ph_3COH: triphenylmethanol; BzAP: benzalacetophenone; TMBzOH: 2,4,6-trimethylbenzyl alcohol; 4NT: 4-nitrotoluene; 4NFB: 4-nitrofluorobenzene; 2,4-DNT: 2,4-dinitrotoluene.

[b] These are H_R indicators; the equivalent pK_{BH+} corresponding to the H_0 scale were obtained from the concentration of H_2SO_4 corresponding to their end points (*14*). Note that two peaks are significant with this indicator.

[c] The neutral forms were obtained in *n*-heptane.

[d] The acid forms were obtained in 95% H_2SO_4, fuming H_2SO_4, or magic acid.

[e] Peak positions were between 200 and 300 nm but they could not be precisely determined. Clearly these determinations did not show the presence of the carbocation (protonated form).

thus indirectly to the H_0 values of solutions of H_2SO_4 at their endpoints.

It has long been known (*14, 21*) that triphenylmethanol readily forms stable carbenium ions on relatively weak acids such as silica–alumina (but not on alumina or on silica gel). This was the strongest and the largest base molecule used in the present work. Figure 5a shows the spectra obtained when this base was adsorbed on catalyst LZ-M8 after various periods of time. The characteristic double-humped spectrum of the triphenylcarbenium ion is readily recognized by the peaks at 410 and 430 nm. The carbenium ion concentration approached its maximum value within the first 30 min and further adsorption was mainly attributable to the neutral form of the indicator. These spectra may be compared with those in Fig. 5b for catalyst HM(7.3) where small amounts of the carbenium ion can be recognized, although much less adsorption took place. These two preparations have similar Si/Al ratios and both behave as solid acids in paraffin-cracking reactions (*5*). The present experiments were carried out under identical conditions. Evidently, for reasons presently unknown, triphenylcarbinol was unable to enter the pore system of HM(7.3) whereas it did enter LZ-M8, at least to a limited extent.

The spectra of Fig. 4 revealed that under

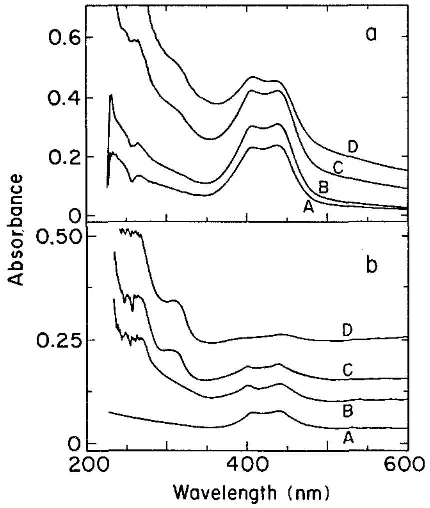

FIG. 5. Absorption spectra from Ph_3C^+ at 30 min (A), 45 min (B), 60 min (C), and 90 min (D) on LZ-M8 (a) and on HM(7.3)

our experimental conditions even much smaller molecules such as *para*-nitrofluorobenzene enter the pore system of HY zeolites rather slowly. Since similar data were available for each spectral determination of the adsorbed indicators (Mode C, Fig. 2), relative rates of removal of the indicators from solution could be obtained from plots of the absorbance of the neutral substrate left in solution vs time. In Fig. 6, such data for Ph_3COH on LZ-M8 are compared with those for HM(7.3). Whereas the latter took up the indicator much more slowly, in neither case was the removal rapid or complete. Only about 17% of the available indicator was adsorbed by HM(7.3) and about 40% on LZ-M8. From the initial concentrations of these solutions, it was estimated that about 0.2×10^{20} and 0.06×10^{20} molec/g were removed from the solutions by LZ-M8 and by HM(7.3), respectively. These coverages were quite low, amounting to only 0.02 Ph_3COH/Al by the former and 0.006 by the latter. Clearly only a small fraction of the potential sites is being sampled by this reagent and this adsorption is presumably at the pore mouths near the outside of the zeolite particles. Interestingly, only a small fraction of these molecules reacted to form the ion, viz., 0.9×10^{-3} and 0.15×10^{-3} Ph_3C^+/Al, respectively.

Similar data for the much weaker base, 4-nitrofluorobenzene, are also plotted in Fig. 6 for several preparations. No adsorption was detectable by HM(7.3) and the uptake was very limited on LZ-M8, which nevertheless had sites which protonated this molecule (Table 2). Interestingly, more of this base was adsorbed on HY(8.1) than on the Nikki silica–alumina catalyst, although neither catalyst protonated it. The data suggest that the results are very much dependent on the strength (irreversibility) of the adsorption.

Previous reaction studies of the cracking of *small* paraffin molecules showed that LZ-M8 and HM(7.3) had similar catalytic activity. Reference to Table 2 shows that the former protonated both 4-nitrotoluene and 4-nitrofluorobenzene. Therefore HM(7.3) presumably has similar acidity, although the indicator tests did not reveal it.

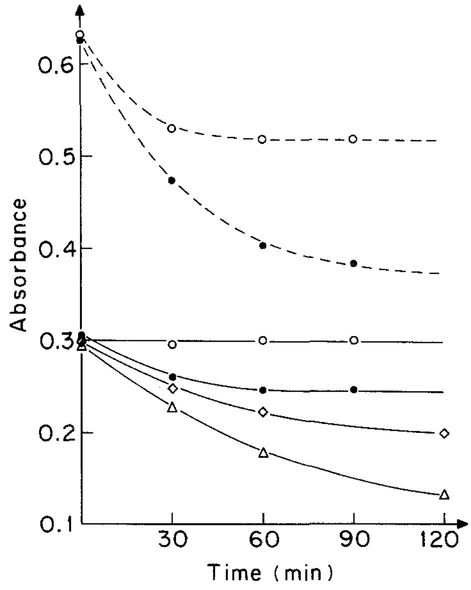

FIG. 6. Disappearance of Ph_3COH (– – –) and 4NFB (——) with time from the solutions in contact with (●) LZ-M8, (○) HM (7.3), (△) HY(8.1), and (◇) LZ-210(12).

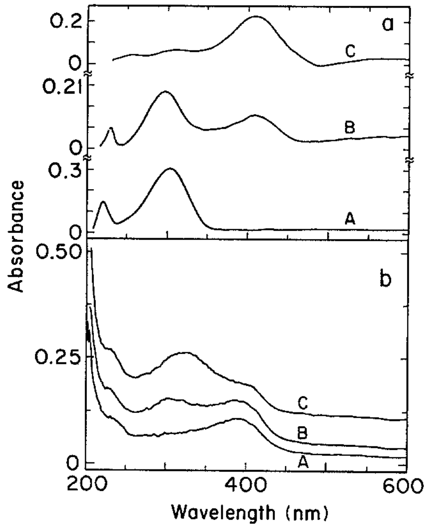

FIG. 7. (a) Absorption spectra of benzylacetophenone in different H_2SO_4–H_2O solutions: Spectrum A: in 52% H_2SO_4 in H_2O; the indicator is present in the neutral form (315 nm); Spectrum B: in 70% H_2SO_4—present in both the neutral form and in the protonated form (415 nm); Spectrum C: in 95% H_2SO_4—present in the acid form only. (b) Absorption spectra of benzylacetophenone on M-46 after 30 min (Spectrum A); 45 min (Spectrum B), and 60 min (Spectrum C).

These results were not modified by use of the ultrasound technique [which is said (*22*) to equilibrate strong basic molecules]. Similar difficulties were encountered when attempts were made to absorb the indicators on H-ZSM-5(39.7). The reason for this is unknown, as in principle even these pores should be large enough to accommodate these molecules.

Spectra from benzylacetophenone in aqueous 52, 70, and 95% H_2SO_4 are shown in Fig. 7a. In agreement with the work of Noyce and Jorgensen (*23*), the two peaks at 315 and 415 nm correspond to the neutral and protonated form of the indicator, respectively. Both peaks were present in the 70% acid, while the indicator was mainly in the protonated form in 95% H_2SO_4 and in the neutral form in 52% H_2SO_4. Related data for the same indicator adsorbed on silica–alumina catalyst M-46 are presented in Fig. 7b. The band for the protonated form appeared first, but subsequent adsorption was mainly in the neutral form. When the catalysts LZ-M8 and JRC-Z-HM(20) were contacted with the same indicator, only the acid form (BH^+) was evident. Similar results were obtained with HY(8.1), LZ-210(12), and LZ-Y82.

The nitrobenzenes required for determination of acidity stronger than 100% H_2SO_4 have both peak maxima (B and BH^+) in the UV region. A yellow color develops when the tail of one of these peaks extends into the visible region above 400 nm. Moreover, in practice the peak from the neutral form shifts to longer wavelengths with increasing acidity, while that for the conjugate acid remains relatively constant. As shown in Table 2, this shift may exceed 50 nm. Consequently, the observation of a yellow color cannot be taken as an indication of acidity strong enough to protonate the indicator. This was demonstrated by the results of experiments where 2,4-dinitrotoluene was added in increasing concentration to 95% H_2SO_4 (Fig. 8). Although this acid is too weak to protonate it, this base produced the yellow color in the solution used for Spectrum B, even though the peak maximum was near 265 nm. These results bring into question claims that certain catalysts show

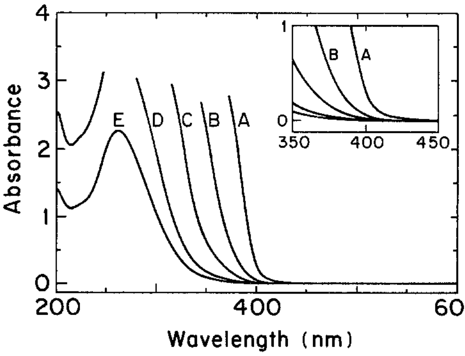

FIG. 8. Absorption spectra of 2,4-dinitrotoluene ($pK_{BH^+} = -13.7$) in 95% H_2SO_4 of different concentrations: (A) 1.6×10^{-2} mol/liter; (B) 3.2×10^{-3} mol/liter; (C) 6.5×10^{-4} mol/liter; (D) 1.3×10^{-4} mol/liter; and (E) 2.5×10^{-5} mol/liter. The light yellow color appeared in the A and B solutions.

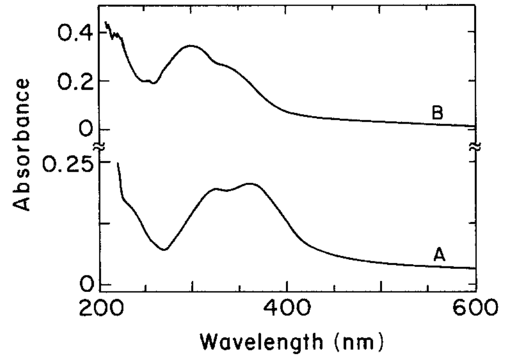

FIG. 9. Acidity tests on LZ-M8 using 4-nitrotoluene ($pK_{BH^+} = -11.3$, Spectrum A) and 4-nitrofluorobenzene ($pK_{BH^+} = -12.4$, Spectrum B). Spectra were recorded after 60 min.

acidity in the range $-18 < H_0 < -13$. Such claims (*24–27*) may or may not be justified and must await further experimentation. The H-mordenites were the strongest acids found in the present work. They were also judged the strongest in our related reaction studies of the cracking of small paraffin molecules (*5*). The spectra of Fig. 9 show bands of both the protonated and neutral forms of 4-nitrotoluene (A) and 4-nitrofluorobenzene (B) on LZ-M8, suggesting that this catalyst has sites in the lower superacid range.

DISCUSSION

A primary objective of the present work was to determine just how strong the acid sites of the H-zeolites (and other solid acids) are and to inquire if any of them qualify as superacids. Moreover, it was desired to evaluate the acidity in terms familiar to chemists. Therefore the H_0 method was adopted and the approach of Walling (*17*) was used. The weakest base was sought which could be protonated by a given surface in the limit of infinite dilution. The spectroscopic results reflected nicely our previous observations on the activities and selectivities in the cracking of isobutane and/or neopentane (*5*) where the acidity could be assessed as follows: LZ-M8 $\approx$ JRC-Z-HM(20) $\approx$ HM(7.3) $\gg$ LZ-Y82 $>$ LZ-210(12) $\approx$ HY(8.1) $\approx$ Beta $\gg$ M-46 $\approx$ Nikki SiO_2/Al_2O_3 $\gg$ silica gel. The H_0 ranges reported here for these materials were: ($-13.7 < H_0 < -12.4$) for the H-mordenites; ($-11.3 < H_0 < -8.7$) for LZ-Y82, LZ-210(12), HY(8.1), and Beta; ($-8.7 < H_0 < -3.3$) for the two silica–alumina catalysts; and $-3.3 < H_0$ for silica gel. Interestingly, the mordenites had acidities just a little higher than 100% H_2SO_4 and hence may be classed as mild superacids while the HY preparations corresponded to about 95% H_2SO_4; the silica–alumina preparations appeared to be much weaker acids, i.e., $\approx$70% H_2SO_4.

Because of the red shifts of the bands of the unprotonated indicators, the appearance of a yellow color on adsorption can be very misleading. Our estimates of the acidity of the silica–alumina catalysts were thus lower than those previously determined by others by visual observation of color for the same or similar preparations. Hirschler (*14*) reported that M-46 contained sites having acidity stronger than 90% H_2SO_4. An even greater discrepancy was found with the work of Hino, Arata and co-workers (*6, 26*) who reported that the (Nikki) silica–alumina had sites equivalent to 99%H_2SO_4 ($-12.7 < H_0 \leq -11.4$). Hattori *et al.* (*25*) concluded that the silica–alumina catalyst protonated 3-nitrochlorobenzene, i.e., had sites in the lower superacid range ($H_0 \leq -13.2$) and Hashimoto *et al.* (*28*) concluded it had sites of $H_0 \approx -13$. The substrate was vacuum transferred in the work of Hattori *et al.* (*25*), but the catalysts were covered with solvent in all the other cases. In separate experiments we found that vacuum transfer of $\approx 10^{14}$ molecules/cm^2 of 4-nitrotoluene onto the dry surface of M-46 produced a distinct yellow color *without protonating* the base. Hashimoto *et al.* attempted to measure acid site distributions by measuring the chemisorption of Hammett indicators from solution without and after poisoning by varying quantities of NH_3. Although their experimental techniques were good, they did not determine the spectra from the adsorbed indicators but assumed that if they were chemisorbed, they must be protonated. We have demonstrated that this is not true and that their conclusion is in error.

Having concluded that spectroscopic determination is essential for any meaningful assay of the catalyst acidity by the indicator method, another problem presents itself. Generally, satisfactory transmission spectra cannot be obtained from the dry solids because of Raleigh scattering. This problem may be alleviated by covering the catalyst platelet with a solvent having a refractive index similar to that of the solid. This solvent may, however, compete with the indicator for the acid sites. Conceivably this would make the acidity appear lower than it actually is. To check on this point, we have substituted benzene or toluene for the *n*-heptane ordinarily used. Relatively small shifts in peak maxima were obtained with the catalysts investigated, but these were insufficient to invalidate any of the conclusions reached. Nevertheless, reflectance spectra from dry solids are needed to confirm this point. We hope to obtain these in the near future.

The problem of how to properly measure catalyst acidity has been under study for many years. These measurements are generally concerned with two properties: estimates of the surface concentration of sites (extensive factor) and their strength (intensive factor). Thus, an acid site distribution is the extensive factor determined as a function of the intensive factor. The literature contains ubiquitous attempts to determine such distributions. Sometimes heats have been measured by differential calorimetry, sometimes by application of the Clausius–Clapeyron equation to adsorption measurements, and sometimes attempts have been made to use TPD measurements from strongly chemisorbed bases such as NH_3 or pyridine to deduce these data. In all of these studies it has been assumed that a broad distribution of site energies exists dependent on the local environments of the sites. In spite of all this work, meaningful quantitative assays have proved largely unsuccessful for a variety of reasons. The first of these is the inability of strong bases such as pyridine, NH_3, or *n*-butylamine (and even Hammett indicators) to equilibrate with the various sites at ordinary temperatures. These molecules are held very strongly where they adsorb first and do not spread uniformly throughout the catalyst bed (*29*). Second, the values of the extensive factor obtained are dependent upon the solvent used (if any) and in some cases the chemisorption leads to decomposition of the base on the catalytic sites. As shown earlier (*30*) some of these problems can be circumvented by first saturating the entire catalyst with the base and then desorbing it to various extents before testing with indicators, but these results may still be in error since the acidity is judged by the appearance of color. Moreover, another problem exists, viz., the adsorption occurs on both Lewis and Brønsted sites and this may have occurred in the present work. It has long been recognized that Lewis acid sites are an important part of the total on silica–alumina catalysts and on HY after dehydroxylation (dealumination) (*31*). Just how such sites affect the spectra is uncertain. Perhaps the Lewis sites can effect shifts of the peak maxima of the unprotonated indicators. Aluminas, which have strong Lewis sites, reportedly do not produce typical colors (or spectra) with either type (*14*).

The above picture may be contrasted with that presented by several workers (*1, 3, 4*) who have suggested that all of the sites of silica-rich zeolites are essentially identical. Recent results from this laboratory (*5c*), dealing with nonlinear effects of NH_3 poisoning on the catalytic rates of cracking of small paraffin molecules, have led us to think that conventional acid site distribution determinations probably do not properly measure an existing distribution of site energies. Instead, it was suggested (*5c*) that each time an NH_4^+ or Na^+ neutralizes an essentially covalent Brønsted site, the acidity (intensive factor) of the remaining sites is reduced by charging up the lattice. Consequently, the apparent distributions, measured using the chemisorption of strong bases, are a result of the integration of this effect with increasing coverage rather than reflecting the actual state of the unperturbed catalyst. If this is so, then the only meaningful measure must involve the use of a probe in such high dilution that the measurement does not perturb the system.

For the present purposes information about the intensive factor is the most germane. Consequently, we have resorted to the qualitative method of Walling (*17*) in which a minimal amount of an indicator is exposed to a large excess of acid surface and the result observed. If the assumption that all of the Brønsted sites of silica-rich H-zeolites are identical is correct, then these measurements should properly reflect their intensive factor and, in addition, provide a measure by which these acids may be compared with familiar liquid acid systems. The H_0 function is a property of the acid only; it is independent of the base. Thus it should be possible to determine the catalyst acidity with the indicator bases and then apply these results to the much weaker hydrocarbon bases. Equation (2) tells us that Eq. (1) will be driven to the right with decreasing H_0. It does not describe the role of the anion in stabilizing the carbenium ion; this is measured by the equilibrium constant of Eq. (1). Nevertheless it follows that both the primary monomolecular initiation steps and the secondary bimolecular chemistry observed in isobutane cracking (*5b*, *5c*) will be accelerated by the increasing acidity as reflected by H_0. Thus, the H_0 method as employed herein has properly ranked the several solid acids in order of their catalytic activity and selectivity, in contrast with the efforts of Jacobs (*32*). Even so, further developments will require the use of smaller molecules of the H_R type (where a stable ion is formed by *reaction* of the molecule with a catalyst proton forming a neutral product such as H_2O). In this way Brønsted acids in the superacid range may be assayed. The present work, like that of Gorte and co-workers (*2*), is a step in that direction. Some of the possible pitfalls have become apparent.

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