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The Effect of Ammonia Adsorption on the Acidity of Silica-Alumina and Alumina Catalysts

The Nature of the Acid Sites*

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Acidic catalysts employed in a number of petroleum refining processes are known to be readily poisoned by basic nitrogen compounds. To throw light on the poisoning process and the nature of the acid sites, the effect of basic nitrogen compounds on the acid strength distribution of silica-alumina and alumina catalysts was determined using H_R as well as H_0 indicators.

Adsorption of NH_3 on M-46 silica-alumina has a pronounced effect on the acid strength distribution with a minor change in the number of sites; on alumina, the situation is reversed. Desorption of NH_3 from silica-alumina at elevated temperatures is accompanied by the loss of a considerable amount of bound water; this should modify the number and strength of the catalyst acid sites. Acid strength distributions derived from high temperature NH_3 desorption data are therefore believed incorrect.

The oxidation of triphenylmethane to the trityl ion in the presence of light and of perylene to the cation radical by silica-alumina are not readily poisoned by nitrogen bases, in contrast to the catalytic activity. This suggests the sites involved are weakly electrophilic and of little catalytic importance. The results favor the view that oxygen under the catalytic influence of Bronsted acids leads to oxidation of these hydrocarbons rather than strong Lewis acids as proposed by several investigators.

Some suggestions relating to the nature of the acid sites on silica-alumina are made based on these experimental data.

INTRODUCTION

Acidic catalysts play a very important role in modern petroleum processing. Reactions such as catalytic cracking, isomerization, reforming, etc., are believed to proceed by a carbonium ion mechanism. Recently (*1*), an improved method for the measurement of the acidity of solid catalysts was described, in which the catalysts are titrated with a nonaqueous solution of *n*-butylamine using a series of H_R indicators. These indicators are converted to carbonium ions by solids of sufficient acid strength.

As is well known, basic nitrogen compounds poison the activity of acid catalysts for the aforementioned reactions. It was therefore of interest to determine the effect of basic nitrogen compounds on the acidity and acid strength distribution of certain catalysts; no data of this type have previously been published. The effect of NH_3 on the acidity of silica-alumina and alumina catalysts was found to be quite different; the significance of these observations with respect to the nature of the acid sites is discussed.

Measurement of the chemisorption of NH_3 as a function of temperature has been suggested as a method for the measurement

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of the acid strength distribution of solid acids (*2–5*). The results of this investigation appear to raise serious questions as to the validity of NH_3 desorption data for drawing quantitative conclusions with respect to the distribution of acid strengths on cracking catalysts. The acid strength distribution of silica-alumina is strongly modified by the chemisorption of NH_3, and in addition the desorption of NH_3 at elevated temperatures is accompanied by the loss of considerable bound water which could alter the number and strength of the acid sites.

The effect of nitrogen bases on the oxidation of triphenylmethane to the trityl carbonium ion and perylene to the cation radical by silica-alumina was also determined. The difficulty with which these reactions are poisoned casts doubt on the suggestion that a few aprotic electrophilic sites are responsible (*6–11*) and favors the view (*12, 13*) that oxygen in conjunction with protonic acids is responsible for the oxidation of these hydrocarbons.

EXPERIMENTAL

Equipment and procedures. The source of the arylmethanol indicators and the *n*-butylamine titration procedure have been described previously (*1*). About 0.05 to 0.1 meq/g indicator was used in measuring end points.

Treatment of catalysts with NH_3 was carried out in 5 × 25-cm Pyrex test tubes fitted with a female standard taper joint. The male joint was fitted with a two-way vacuum stopcock and standard taper joint for attachment to a vacuum line equipped with a molecular sieve trap and capable of reaching 10^{-6} torr. A short 5-mm side tube fitted with a serum cap was attached to the tube near the joint; NH_3 was admitted to the activated and evacuated catalyst by gas syringe through this side tube or in some cases through the stopcock.

Catalysts. The M-46 is a commercial silica-alumina (SA) catalyst containing about 12% alumina and obtained from the Houdry Process Corporation. The surface area was 280 m^2/g. RD-150 is a commercial Baker-Sinclair platinum-alumina reforming catalyst.

RESULTS

Effect of evacuation temperature on acidity of NH_3-saturated M-46 and RD-150. Three different portions of the same batch of M-46 were activated by evacuation at 450°, then saturated with NH_3 at room temperature and atmospheric pressure, and pumped under high vacuum for 18 hr at temperatures of 100°, 200°, and 300°C, respectively. These three catalysts were titrated with *n*-butylamine to measure the acid strength distribution; the results are given in Table 1.

TABLE 1

ACIDITY OF NH_3-SATURATED M-46 AS A FUNCTION OF EVACUATION TEMPERATURE

	Acidity, meq/g stronger than H_2SO_4 concentration given in Column I		
Evacuation temperature:	100°C	200°C	300°C
Carbonium ion indicators			
1.2% H_2SO_4	0.21	0.27	0.315
36% H_2SO_4	0.11	0.19	0.23
50% H_2SO_4	0.04	0.16	0.19
68% H_2SO_4	0.0	0.11	0.19
77% H_2SO_4	0.0	0.0	0.14
Hammett indicators			
3×10^{-4}% H_2SO_4	0.16	0.19	0.22
48% H_2SO_4	0.14	0.17	0.22
72% H_2SO_4	0.10	0.14	0.20
90% H_2SO_4	0	0.11	0.17
$(C_6H_5)_3CH$	0[a]	0.11	0.19
Perylene	0.04[a]	0.14	0.17

[a] Data for $(C_6H_5)_3CH$ and perylene are the additional *n*-butylamine required to poison chemisorption as cation or cation radical.

The Hammett indicators suggest the presence of considerably more relatively strong acidity than do the carbonium ion indicators, particularly at 100°C. It is known that even at 200°C M-46 retains enough chemisorbed ammonia to poison nearly all of its catalytic activity. While data on the amount of H_R acidity stronger than 88% H_2SO_4 were not obtained, a plot of the data in Table 1 at each acid strength level vs. the temperature of heating makes it clear that very little if any acidity of this strength would be recovered at 300° and that even at 400° recovery would be incomplete. Therefore, our method of measuring acidity with H_R indicators is certainly more in accord with the catalytic activity than data obtained with Hammett indicators.

RD-150 was similarly saturated with NH_3, and the acidity measured by *n*-butylamine titration after evacuation at the same three temperatures. The results of these titrations are given in Table 2.

TABLE 2
Acidity of NH_3-Saturated RD-150 as a Function of Evacuation Temperature

	Acidity, meq/g stronger than H_2SO_4 concentration given in Column I		
Evacuation temperature:	100°	200°	300°
Carbonium ion indicators			
1.2% H_2SO_4	0	0.28	0.59
36% H_2SO_4	0	0.28	0.59
50% H_2SO_4	0	0	0.55
Hammett indicators			
3×10^{-4}% H_2SO_4	0	0.32	0.59
48% H_2SO_4	0	0.32	0.59
72% H_2SO_4	0	0.32	0.59
90% H_2SO_4	0	0.32	0.59

The change in catalyst acidity brought about by the presence of NH_3 is a measure of the extent of chemisorption on acid sites which are measured by the acidity titration, though it may not necessarily be directly proportional to the weight of NH_3 chemisorbed. Chemisorption on sites which do not affect the indicators is also a possibility. Table 3 compares M-46 and RD-150 on the basis of the percentage of the original acidity restored at each temperature and for each indicator.

When pumped at 100°C, even the weakest acidity of RD-150 is absent, while M-46 has recovered much of its weak acidity. At 300°, RD-150 has recovered nearly all of its acidity while M-46 still lacks 26% of its >77% H_2SO_4 carbonium ion acidity and most of its >88% H_2SO_4 H_R acidity (see discussion of Table 1). These data are significant, for they indicate that ammonia is held more strongly at the strong H_R acid sites of M-46 than on Al_2O_3 acid sites. Hammett indicators suggest that all of the acidity of RD-150 is stronger than 90% H_2SO_4. H_R indicators therefore

TABLE 3
Chemisorption of NH_3 at Elevated Temperatures by RD-150 and M-46

	Percentage recovery of original acidity after NH_3 neutralization and evacuation					
	100°C		200°C		300°C	
	M-46	RD-150	M-46	RD-150	M-46	RD-150
Carbonium ion acidity stronger than:						
1% H_2SO_4	60	0	77	47	90	100
36% H_2SO_4	41	0	71	47	85	100
50% H_2SO_4	18	0	73	0	86	93
68% H_2SO_4	0	—[a]	53	—	90	—
77% H_2SO_4	0	—[a]	0	—	74	—
Hammett acidity stronger than:						
3×10^{-4}% H_2SO_4	64	0	76	54	100	100
48% H_2SO_4	56	0	68	54	100	100
72% H_2SO_4	40	0	67	54	95	100
90% H_2SO_4	0	0	58	54	94	100
$(C_6H_5)_3CH$[b]	0	—	52	—	90	—
Perylene[b]	19	—	67	—	81	—

[a] RD-150 initially has no carbonium ion acidity stronger than 68% H_2SO_4.

[b] Data for $(C_6H_5)_3CH$ and perylene are based on the *n*-butylamine titer required to poison chemisorption as cation or cation radical.

appear to indicate the relative acid "strength" of these two catalysts; Hammett indicators do not.

It should be pointed out, however, that it may not be necessarily correct to define acid strength in terms of NH_3 retention if, as seems probable, the acid sites of alumina and SA are of different types.

The acidites of M-46 and RD-150 partially poisoned with NH_3 differ in another important respect. The poisoned RD-150 exhibits substantially no distribution of acid strengths. On the other hand, the poisoned M-46 shows a steeper acid strength distribution than before NH_3 addition, with strong acids being eliminated and being replaced in part with weaker acid sites not originally present. This is more clearly evident in Fig. 1 where the amount of carbonium ion acidity in each range of acid strength is shown.

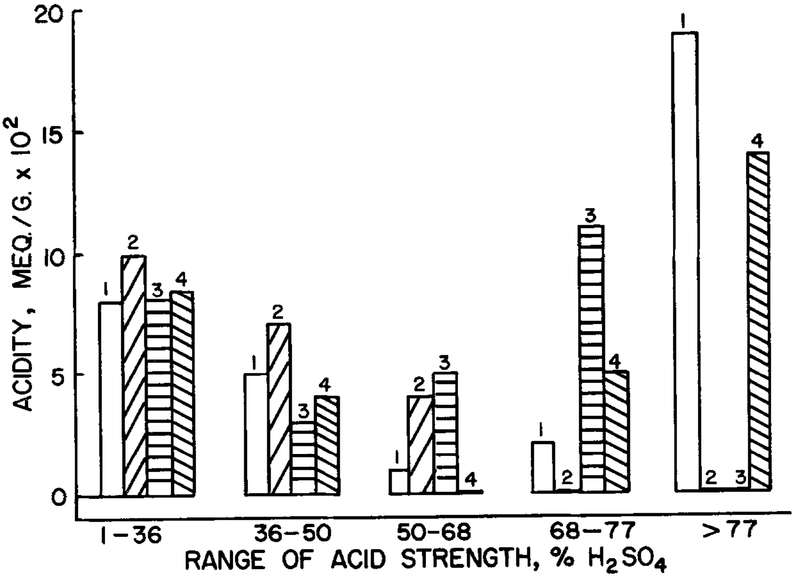


FIG. 1. Effect of NH_3 on acid strength distribution of M-46. (1), unpoisoned M-46. M-46 saturated with NH_3 and evacuated at temperatures of (2) 100°; (3) 200°; and (4) 300°.

Ammonia chemisorption is seen to have little effect on the amount of weak acidity, but the amount of intermediate strength acidity increases while the strong acidity decreases. It is unfortunate that the H_R indicator corresponding to 88% H_2SO_4 was not employed at the time these data were obtained, for the data in Tables 1 and 5 indicate the probability that at 300° a large part of this strong acidity would remain poisoned. Acidity of this strength may be important in catalytic reactions.

Ammonia chemisorption by M-46 and RD-150 as a function of temperature. In order to measure the weight of NH_3 chemisorbed as a function of temperature, 10 to 14 g of 60–140 mesh catalyst was activated by evacuation at 450°C, weighed, reevacuated at 450° to remove any water picked up during weighing, then saturated with anhydrous NH_3 at 0°C. The catalysts were pumped overnight to 10^{-5} mm pressure at several increasing temperatures and weighed. The results are summarized in Table 4.

Unfortunately, when the catalysts were evacuated at temperatures of 400° or above, the weight was found to be appreciably less than before the NH_3 was added. These data are reported in Table 4 as negative NH_3 adsorption values (Series 1). Apparently, in the course of pumping off NH_3, water of constitution is removed be-

TABLE 4
AMMONIA CHEMISORPTION BY M-46 AND RD-150 AS A FUNCTION OF TEMPERATURE

Evacuation temperature	Apparent NH_3 adsorption (meq/g)			
	M-46		RD-150	
	Series 1	Series 2	Series 1	Series 2
30°	0.40	—	1.09	—
100°	0.21	—	0.66	—
200°	0.10	—	0.40	—
300°	0.015	0.11	0.18	0.15
375°	—	—	—	0.046
400°	−0.05	−0.016	—	—
450°	−0.14	−0.038	−0.04	−0.056

low 300° which could not be pumped off at 450° during activation of the catalyst. The RD-150 was pumped 3 days at 450° before adding the NH_3 to ensure that equilibrium was attained.

At the completion of Series 1, the residual catalyst was again saturated with NH_3 and the process repeated. The apparent NH_3 adsorption values in Series 2 are based on the weight of catalyst after completion of Series 1, not on the original weight. Again, negative "adsorption" values show that for both M-46 and RD-150 the presence of NH_3 has catalyzed an additional loss of water of constitution.

It is possible to obtain from these data only a rough estimate of the quantities of NH_3 retained at 100°, 200°, and 300° to correspond with the acidity measurements in Tables 1–3. At 100°, both M-46 and RD-150 retain an amount of NH_3 equivalent to the strong acidity as measured by butylamine titration. At 300° M-46 retains about 0.11–0.13 meq/g of NH_3 while RD-150 retains 0.15–0.18 meq/g. In raising the temperature from 100° to 300°, M-46 has lost about ½ of the NH_3 chemisorbed, while RD-150 has lost ¾.

In view of the fact that at 300° RD-150 has recovered substantially all of its original acidity (Table 3), it is somewhat surprising to find as much as 0.15 meq/g of NH_3 still present. The 60–140 mesh catalyst used for the chemisorption measurement may lose NH_3 less readily than the about 200-mesh particles used for the titration data; nevertheless, RD-150 appears to retain some NH_3 at 300° in a form which is not chemisorbed at the acid sites. It would be of interest to obtain additional information on the manner of binding this tightly held NH_3. One possibility is that it is held as NH_2^- groups as suggested by Peri (*14*) on the basis of infrared evidence; SA may also bind NH_3 as NH_2^-.

Effect of temperature of reaction on the chemisorption of NH_3 by silica-alumina. When a limited amount of NH_3 (equivalent to about half of the strong acidity) is added to M-46, the acid strength distribution is strongly affected by the temperature at which the ammonia is equilibrated before measurement of the acidity. The catalyst was activated at 450°C in vacuum, 0.1 meq/g of NH_3 added by syringe at room temperature to the evacuated tube and the catalyst equilibrated in the closed tube at the desired temperatures. After equilibration, the pressure was brought up to atmospheric with dry nitrogen, and the catalyst removed for titration.

When the NH_3 is added at room temperature, even the strong carbonium ion acidity is reduced by only 20–30% of the amount of NH_3 added (Table 5). Heating to 300° for 10 hr has little effect on the H_R acidity weaker than 68% H_2SO_4 but greatly reduces acidity stronger than 77% H_2SO_4. Heating to a temperature of 65° for 1 hr reduces the strong acidity considerably more than heating to 300°. At both 65° and 300° the loss in H_R acidity $>$ 88% H_2SO_4 is more than the amount of NH_3 added; at 65° the loss in acidity $>$ 77% H_2SO_4 also exceeds the amount of NH_3 used.

Included in Table 5 are the results of an experiment in which the M-46 was first equilibrated at 100°C with 0.1 mmole/g of added water before adding NH_3 and equilibrating overnight at room temperature. The loss in strong acidity is several times as great as with NH_3 alone equilibrated at room temperature but the effect on strong acidity is much less than for the M-46 equilibrated with NH_3 alone at 65° or 300°. The added water resulted in no change in the H_R acidity as strong as 1.2 or 36% H_2SO_4; thus there is no indication

TABLE 5

EFFECT OF EQUILIBRATION TEMPERATURE ON THE ACIDITY OF M-46 PARTIALLY NEUTRALIZED WITH 0.1 MEQ/G NH_3

	H_R acidity, meq/g stronger than H_2SO_4 conc. in Column 1				
Temperature of equilibration:	$H_2O + NH_3$[a] 30°	30°	65°[b]	300°	No NH_3
Acid strength (wt % H_2SO_4)					
1.2	0.33	0.33	0.32	0.34	0.35
36	0.23	0.23	0.23	0.23	0.27
50	0.17	0.19	0.21	0.21	0.22
68	0.16	0.18	0.135	0.19	0.21
77	0.13	0.17	0.02	0.13	0.19
88	0.10	0.17[c]	0	0	0.19
Triphenylmethane[d]	0.15	0.18	0.19	0.17	0.21
Perylene[d]	0.17	0.17	0.14	0.17	0.21

[a] Catalyst equilibrated with 0.1 mmole H_2O/g at 100°C for 1 hr, then cooled and NH_3 added and equilibrated at room temperature.

[b] A different batch of M-46 prepared from the same lot number was used in this experiment; other data obtained on different portions of a single batch of ground M-46.

[c] Even with no $BuNH_2$ added, the color produced with this indicator was relatively faint, so that the end point in the titration is less definite than usual.

[d] Data for $(C_6H_5)_3CH$ and perylene are the additional *n*-butylamine required to poison chemisorption as cation or cation radical.

that additional Bronsted acidity stronger than 1.2% H_2SO_4 has been created by hydration of Lewis sites.

The small effect of adding NH_3 at room temperature on the butylamine titer is worthy of further investigation. One possibility considered was that as neutralization by butylamine approaches completion, the NH_3 is displaced from the acid sites and lost by volatilization. Experiments showed, however, that any such loss of NH_3 is negligible.

Activated M-46 containing some triphenylcarbinol as indicator was placed in a tube closed with a ground joint and stopcock, the tube evacuated, and anhydrous NH_3 added to a pressure of about 500 mm. Upon heating the closed tube to 300°, a strong yellow color characteristic of the trityl ion developed; cooling resulted in complete decolorization. This experiment shows that considerable H_R acidity stronger than 50% H_2SO_4 exists on silica-alumina at 300° even in the presence of a large excess of NH_3 at >500 mm pressure, and that a relatively high concentration of trityl carbonium ions is present on the catalyst under these conditions.

The catalyst above was cooled to room temperature and pumped under high vacuum while slowly raising the temperature. At 50°C the yellow color of the carbonium ion returned, showing that below 50° acids stronger than 50% H_2SO_4 react completely with NH_3 even at very low NH_3 pressure. This experiment also shows that catalyst sites able to convert triphenylcarbinol to the cation can be partially freed of NH_3 at a temperature as low as 50°, which appears inconsistent with the view of Leftin and Hall (*6*) that $5 \times 10^{12}/cm^2$ strong Lewis sites are responsible for this reaction. The data in Table 4 indicate at least 7×10^{13} NH_3 molecules/cm^2 would be adsorbed at 50° and that almost 350° is required to reduce NH_3 chemisorption to a level of $5 \times 10^{12}/cm^2$.

Effect of quinoline chemisorption at 300° on acidity of silica-alumina. Quinoline was added to M-46 and the catalyst heated at 300°C for 3 hr in a stream of nitrogen to remove physically adsorbed quinoline. The conditions were similar to those used by Mills *et al.* (*15*) for measurement of catalyst acidity by "quinoline number"; at 315° M-46 was reported to chemisorb about

0.06 meq/g of quinoline. Titration of the poisoned catalyst is summarized in Table 6.

TABLE 6

ACID STRENGTH DISTRIBUTION OF M-46 WITH QUINOLINE CHEMISORBED AT 300° AND ROOM TEMPERATURE QUINOLINE TITER OF UNPOISONED M-46

Acid strength (wt % H_2SO_4)	Acidity, meq/g ($BuNH_2$ titer) stronger than given H_2SO_4 conc.	Room temperature quinoline titer (meq/g)
H_R Indicators		
1.2	0.27	18
36	0.22	1.21
50	0.08	0.17
68	0.02	0.09
77	0	0.09
H_0 Indicators		
3×10^{-4}	0.22	1.21
48	0.19	1.09
72	0.08	0.63
90	0.04	0.10
$(C_6H_5)_3CH$	0.04[a]	0.12
Perylene	0.08[a]	0.17

[a] Additional *n*-butylamine required to poison chemisorption as cation or cation radical.

The strong acidity was found to be somewhat greater than for M-46 + NH_3 heated to 100°, but well below that for the NH_3-poisoned catalyst heated to 200°. In view of the fact that quinoline is a much weaker base than NH_3 its much greater poisoning effect probably results in part from its considerably lower vapor pressure.

As in the case of NH_3, chemisorbed quinoline causes only a modest reduction in the total number of acid sites but strongly modifies the acid strength distribution. Acid sites stronger than 77% H_2SO_4 are eliminated and the number of relatively weak sites greatly increased. Since it has been found that cumene cracking activity correlates with acidity stronger than 77% H_2SO_4 (*1*), the lack of catalytic activity reported by Mills *et al.* (*15*) is understandable even though the acidity has not all been neutralized.

Quinoline titers of M-46 at room temperature were obtained using a standard solution of quinoline in benzene; the results for a variety of indicators are given in Table 6. The acidity stronger than 77% H_2SO_4 using quinoline as titrant is less than half the value obtained by *n*-butylamine. Thus at least the greater part of the discrepancy between quinoline numbers and other measures of acidity is not due to a change in the number of acid sites with temperature. The difference between butylamine and quinoline titers is probably of steric origin: The quinoline molecule because of its large size (~15 Å diameter) is able to cover or block two or more acid sites. This conclusion is supported by data on the titration of a variety of catalysts with amines of varying steric demand (*16*); the titer decreases consistently with increasing size of the amine. Therefore, it is possible to derive information relative to the spacing of acid sites from such titration data.

The data in Table 6 also show that quinoline because of its weak basicity does not very effectively neutralize H_R acidity much weaker than 50% H_2SO_4.

Effect of nitrogen bases on chemisorption of triphenylmethane and perylene. The chemisorption of these substrates was studied on our poisoned M-46 catalysts to help elucidate conflicting views on whether nonprotonic or protonic sites are responsible. It has been proposed that $5 \times 10^{12}/\text{cm}^2$ aprotic Lewis sites are responsible for the chemisorption of $(C_6H_5)_3CH$ on SA by hydride abstraction (*6*), and that these same Lewis sites chemisorb perylene as the cation radical (*7–9*). Very recently, Porter and Hall (*11*) propose $6 \times 10^{11}/\text{cm}^2$ aprotic electrophilic sites chemisorb $(C_6H_5)_3CH$ in the dark; they suggest the remaining $4.4 \times 10^{12}/\text{cm}^2$ aprotic sites convert $(C_6H_5)_3COH$ to the trityl ion, and many of them are able to chemisorb $(C_6H_5)_3CH$ in the presence of light. Hirschler and Hudson (*12*), working under conditions where the photolytic reaction predominated, suggested that $(C_6H_5)_3CH$ is oxidized to $(C_6H_5)_3COH$ or $(C_6H_5)_3COOH$ which is converted to the trityl ion by Bronsted sites; and that chemisorbed oxygen accepts an electron from perylene in the presence of strong proton acids. Recent evidence suggests oxygen may instead catalyze electron transfer to proton acids (*13*).

With one exception, all of the poisoned catalysts chemisorbed both substrates. Butylamine titers were obtained using $(C_6H_5)_3CH$ and perylene indicators as previously described (*12*) in order to determine the additional amount of base needed to poison the chemisorption. All samples were exposed to room daylight, so photolytic chemisorption of $(C_6H_5)_3CH$ is involved. The data are included in Tables 1, 5, and 6. The numbers obtained, compared to those observed for the unpoisoned catalyst, are a measure of the degree to which NH_3 or quinoline have poisoned the sites responsible for oxidation of these hydrocarbons.

The $(C_6H_5)_3CH$ reaction is completely poisoned on the 100° evacuated catalyst (Table 1); at 200° the titer is about half recovered, and at 300° the titer is only slightly less than for unpoisoned M-46. Perylene behaves similarly except that conversion to the cation radical is not completely poisoned even on the 100° catalyst.

The effect of equilibrating 0.1 meq/g of NH_3 ($2 \times 10^{13}/cm^2$) with M-46 at various temperatures (Table 5) is to reduce the titer with $(C_6H_5)_3CH$ indicator by only 0.02–0.04 meq/g; varying the equilibration temperature has no appreciable effect, although it markedly affects the very strong acidity. The total base ($NH_3 + BuNH_2$) needed to poison the reaction exceeds $4.5 \times 10^{13}/cm^2$ or 9 molecules per electrophilic site in each case. The greatest effect on perylene oxidation (0.07 meq/g) is observed for the catalyst equilibrated at 65°, which has the least strong acidity. This fact suggests that acidity stronger than 77% H_2SO_4 promotes perylene oxidation more than oxidation of $(C_6H_5)_3CH$. This is in accord with the proposal (*13*) that a strong proton acid is the electron acceptor.

Equilibrating 0.1 mmole of water ($2 \times 10^{13}/cm^2$) with the M-46 prior to adding the $2 \times 10^{13}/cm^2$ of NH_3 at room temperature had only a small effect on the oxidation of $(C_6H_5)_3CH$ and none on the oxidation of perylene.

Since the chemisorption of $(C_6H_5)_3CH$ in the dark may proceed by a different mechanism than the photolytic reaction (*11*), the resistance to poisoning of the dark reaction was tested by saturating 0.5 g of M-46 (activated at 500° in air) with NH_3 at atmospheric pressure (no acidity remained by indicator test), then evacuating overnight at 125° and 10^{-2} mm pressure with 2–3 g of unpoisoned M-46 placed in the cold end of the chamber. Reaction of the poisoned M-46 with 2 g/liter $(C_6H_5)_3CH$ in benzene overnight at room temperature in the dark developed a moderately strong yellow color indicative of chemisorption. From the data of Table 4 almost 4×10^{13} NH_3/cm^2 would be chemisorbed at 125°, over 60 times the number of sites able to chemisorb $(C_6H_5)_3CH$ in the dark (*11*).

The need for $4 \times 10^{13}/cm^2$ or more molecules of base to poison chemisorption of $(C_6H_5)_3CH$ even after half this amount of NH_3 had been equilibrated at 300°; and the ease with which NH_3 is desorbed from sites able to chemisorb this substrate even in the dark are inconsistent with the view (*6, 11*) that strongly electrophilic aprotic sites are involved. Strong Lewis acids usually form 1:1 complexes with strong Lewis bases. SA has many sites capable of retaining NH_3 at 515° (*14*). It seems very unlikely that an aprotic site sufficiently electrophilic to convert $(C_6H_5)_3CH$ or $(C_6H_5)_3COH$ to the carbonium ion (*11*) would not be readily poisoned by stronger and much smaller bases such as NH_3. Generation of carbonium ions by protonic sites, however, requires only relatively weak acidity (50% H_2SO_4), and a considerable amount of base is required to lower the acidity of M-46 to this level (*1, 12*). In 50% H_2SO_4 there are many water molecules available for each hydrogen ion present, i.e., many molecules of a Lewis base may be required to lower the acid strength of a proton to this level.

The views of Hall and co-workers (*6, 11*) that aprotic electrophilic sites generate carbonium ions from $(C_6H_5)_3COH$ and other arylmethanols, and that $6 \times 10^{11}/cm^2$ of the most strongly electrophilic sites on SA abstract hydride ions from triphenylmethane in the dark (*11*) apparently cannot both be correct. A NH_3-poisoned M-46 evacuated at 200° is unable to generate carbonium ions from diphenylcarbinol (Table 1, 77% H_2SO_4), which would point to the absence of strong electrophilic sites. Yet NH_3-poisoned M-46 evacuated at only 125°, with even weaker acid sites, is able to generate trityl ions from triphenylmethane in the dark.

If as proposed (*7–8*) aprotic Lewis sites are responsible for removing an electron from perylene, the large excess of base should have poisoned the reaction. The data tend to support the conclusion (*12, 13*) that oxidation by chemisorbed or lattice oxygen along with protonic acids accounts for these reactions rather than hydride ion or electron abstraction by strong Lewis acids.

The catalytic sites on SA are readily poisoned by nitrogen bases (*15, 17, 18*) in contrast to sites active in oxidation of $(C_6H_5)_3CH$ and perylene, indicating such sites may be of less catalytic importance than originally supposed (*6*). It is possible, however, that a strong protonic site of high activity is, when partially poisoned with NH_3, still able to take part in the oxidation of these substrates but no longer catalytically active (*12*). Partial poisoning of an aprotic Lewis site in this manner seems unlikely.

DISCUSSION

Measurement of Acid Strength Distribution by NH_3 Chemisorption

Several investigators (*2–5*) have proposed that the acid strength distribution of solid acids can be determined by measurement of the desorption of NH_3 as a function of temperature. Kubokawa (*5*) measured the activation energy for NH_3 desorption from SA as a function of temperature, and reported that the energy distribution of sites as measured by NH_3 desorption differed markedly from that inferred by *n*-butylamine titrations using Hammett indicators. Addition of 0.1 meq/g of NH_3 to M-46 (Table 5) does not significantly change the *total* number of acid sites measured by titration, but in effect converts very strong sites to weaker ones. Thus, *as measured by indicator titration* a partially poisoned SA has a heterogeneous distribution of site energies in qualitative agreement with the desorption data of Kubokawa. This suggests a possibility that at the same NH_3 content the indicator titration and desorption methods could be in substantial quantitative agreement. However, the site-energy distribution of the unpoisoned catalyst cannot be derived from ammonia desorption measurements. The procedure of Misono *et al.* (*19*) is also open to the objection that the site-energy distributions obtained are not characteristic of the unpoisoned catalyst because the adsorbed pyridine modifies the acid strength.

As shown in Table 4, NH_3 catalyzes the loss of water of constitution at temperatures as low as 250–300°, which may alter the number and type of acid sites. Also, after heating with NH_3 to elevated temperatures, it may not always be correct to equate the amount of tightly held NH_3 to acidity. Thus, at 300°, RD-150 has recovered substantially all its acidity (Table 3) while retaining 0.15 meq/g of NH_3.

Wilmot *et al.* (*20*) reported that acidity as measured by ammonia chemisorption did not correlate with the selectivity and activity of solid acid catalysts for olefin isomerization. The three effects noted above may explain the lack of correlation found, indeed they would suggest that a correlation would be unlikely. The possibility still exists that acidity as measured by some other more suitable technique, perhaps by H_R indicator titration, would be found to correlate with the catalytic activity.

Poisoning of Catalytic Activity by Nitrogen Bases

Mills *et al.* (*15*) showed that an exponential relation existed between the amount of nitrogen base added to SA and the activity for cumene cracking. In the case of quinoline, 0.007 meq/g reduced the amount of cracking to 50% of the initial value whereas 8.5% of the initial activity remained after adding 0.03 meq/g. This exponential dependence is in at least qualitative accord with our observations on the effect of nitrogen bases on the H_R acidity of M-46 and the observation (*1*) that cumene cracking on SA depends upon H_R acidity stronger than 77% H_2SO_4. In Table 5 it is seen that heating M-46 with 0.1 meq/g of NH_3 has caused the disappearance of 0.19 meq/g of acidity stronger than 88% H_2SO_4. Inspection of the data at 65° suggests that considerably less than 0.1 meq/g of NH_3 would have sufficed to eliminate all of the H_R acidity stronger than 88% H_2SO_4.

Mills *et al.* (*15*) also found that quinoline poisoned SA for the cracking of gas oil to a lesser degree than it did for cumene cracking. If one makes the reasonable assumption that a portion of the gas oil is more easily cracked than cumene, this observation is in accord with a heterogeneous site-energy distribution. Thus, the catalytic observations of Mills *et al.* as well as the desorption data of Kubokawa (*5*) provide some support for our findings employing H_R indicator titrations with respect to the heterogeneous site distribution of nitrogen-poisoned SA.

In view of the observation (Table 5) that one NH_3 molecule appears capable of destroying several very strong acid sites, and the exponential relation between amount of nitrogen base added and catalytic activity, attempts to count the number of acid sites active in a given reaction by progressive poisoning with nitrogen bases must be viewed with considerable caution, at least for SA. This same effect may result in a significantly lower number of NH_4^+ or pyridinium ions on a catalyst (*21–23*) than the number of strong protonic sites originally present. This nonstoichiometric effect, as well as a steric effect, may explain why "quinoline numbers" (*15*) are considerably less than acidities measured by other methods.

The possibility that this nonstoichiometric effect could influence acidities measured by butylamine titration must also be considered. However, the data in Table 5 show that NH_3 at room temperature had very little effect on the acid strength distribution and the same is probably true of *n*-butylamine. The data in the last column of Table 5 for unpoisoned M-46, where most of the acidity is very strong, also indicate that very little reaction of butylamine with the catalyst in such a way as to modify the acid strength distribution took place. Even moderate heating could result in reaction of butylamine with modification of acid strength distribution; the use of ultrasonic energy to speed equilibrium as suggested by Bertolacini (*24*) in some circumstances might cause sufficient local heating to modify the acid strength distribution.

Nature of the Acid Sites

The nature of the active acid sites on SA has been a subject of controversy for many years, some workers regarding them as Bronsted acids while others view them as nonprotonic Lewis acids (*25*). A number of arguments in favor of the Bronsted view were presented previously (*1, 12*). The fact that the effect of NH_3 chemisorption on the acidity of M-46 and RD-150 is so completely different adds weight to the view (*12*) that the acid sites differ so greatly as to suggest they are not aprotic Lewis sites of different strength but that those on M-46 are protonic. The behavior of RD-150 toward NH_3 is about what would be expected from Lewis-type sites. Peri (*14*) was unable to detect any NH_4^+ ions by infrared measurements on alumina containing chemisorbed NH_3; addition of H_2O does not convert pyridine to pyridinium ion on Al_2O_3 as it does on SA (*21, 23*).

Ion exchange of M-46 with alkali metal ions produces an effect on the H_R acid strength distribution similar to that noted above for chemisorbed ammonia, i.e., a moderate degree of exchange does not greatly affect the total number of acid sites but produces a heterogeneous distribution of acid strengths (*1*). This suggests that much of the chemisorbed NH_3 is present in a form resembling the ammonium ion, since there are many similarities in the chemistry of ammonium and alkali metal ions.

Ion exchange of SA with a metal cation is commonly regarded as a replacement of a proton by the metal ion, and on the basis of this simple or classical picture, one would expect the protonic acidity to disappear and the hydrogen content to be reduced in proportion to the degree of exchange. Instead, the effect on acidity as measured by H_R indicators is replacement of the strong acid sites by ones of intermediate strength (*1*). It is now reported that nitrogen bases primarily modify the site-energy distribution rather than the number of acid sites. Ion exchange apparently leads not to replacement of the proton but to attachment of the metal ion to the site in such a way that the acid strength is reduced. The reduction in acid strength is related to the size and polarizability of the metal ion (*1*). These observations strongly suggest it is incorrect to assume that the number of protonic sites is necessarily measured by the change in hydrogen content on ion exchange (*26, 27*).

The Bronsted site observed in reactions of liquid acids is usually that of a highly solvated proton. On a well-dehydrated catalyst the proton is probably attached to a single oxygen atom and the acidity is the result of the fact that this bond is electron-deficient. Thus, the Lewis or electrophilic nature of the proton may be more prominent than in liquid Bronsted acids, and the proton may not be readily transferred completely to a substrate as in the case of a highly solvated proton. One indication of this electrophilic character is recent evidence that strong proton acids are the electron acceptors in conversion of aromatic molecules to radical ions (*13, 28*). Thus, one may suppose that NH_3 or pyridine may hydrogen-bond to this electrophilic hydrogen without resulting in a free or classical ion. Solvation by addition of H_2O may then facilitate actual proton transfer to form a pyridinium ion, or hydrogen transfer from catalyst to reactants. In effect, the electrophilic catalyst hydrogen may remove an OH^- from H_2O, freeing a proton. In a sense, this could be viewed as stabilizing the ion by solvation.

Basila, Kantner, and Rhee (*21*) proposed that the primary acid sites on silica-alumina are of Lewis type centered on surface Al atoms. Most of their experimental observations, and the butene isomerization data of Ozaki and Kimura (*29*) can be explained on the basis that the postulated Lewis site is the hydrogen atom of an unsolvated strongly acidic OH group. An olefin adsorbed on this site would be converted to a carbonium ion which could more easily donate one of its own protons to another reactant molecule than transfer the catalyst proton. Since alumina does not have strong H_R acidity, the above postulate would rationalize the differences in behavior between alumina and SA on adding H_2O, which Basila *et al.* (*21*) were admittedly unable to do on the basis of their proposal. Additional details as well as experimental evidence in support of this suggestion will be given in a forthcoming paper.

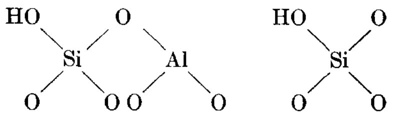
Hall and co-workers (ref. *30*, and prior papers cited therein) have placed very small upper limits on the number of Bronsted sites in SA on the basis of tracer experiments. These numbers are arrived at on the basis of an *assumed* mechanism in which the catalyst proton is completely transferred to substrate. The above considerations indicate this need not be so; a proton on a solid well-dehydrated catalyst may behave differently from a solvated proton in a liquid medium. At any rate, until the actual detailed mechanism is known, one cannot make a definitive calculation of the number of protonic sites from such data. In addition, not all protonic sites would be equally active in a given reaction, especially when small slugs of reactant are used. We do not suggest that titration data give a definitive value for the number of protonic sites.

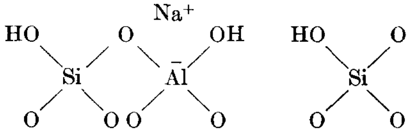
Flockhart and Pink (*10*) found the oxidation of perylene on SA is reduced stepwise to a low value by three successive base exchanges, which they interpreted as showing that Lewis sites are responsible. However, these data could be equally well explained by either of the two pictures involving protonic acids and oxygen (*12, 13*) since the H_R acidity stronger than 50% H_2SO_4 was also reduced stepwise to a low value. The present and earlier (*12*) data show that on a variety of catalysts perylene oxidation is poisoned below 50% H_2SO_4 H_R acid strength $[(C_6H_5)_3COH]$. It is well-documented that the oxidation of aromatics to radical ions is strongly influenced by oxygen (*7, 9, 11, 12, 31–33*).

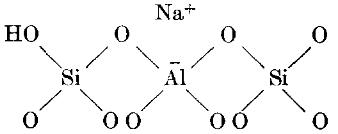
A Tentative Model of the Acid Site

The ability of one NH_3 molecule to affect more than one site and the fact that the quinoline titer is less than one-half that for *n*-butylamine suggest that acid sites do not occur singly as isolated points on the surface but only in relatively closely spaced clusters where a particular type of local order exists. This local order could consist of a network of alternating silicon and aluminum atoms connected by oxygen bridges such as is present in the X zeolite. Ordering of this type would extend over a limited distance, too small to be detected by X-ray diffraction, but still of sufficient extent that suitable areas would be relatively infrequent, in line with the finding by Mills *et al.* (*15*) that 4% coverage of the surface by quinoline completely poisons activity. The silicon and aluminum atoms could be joined in six-membered rings as in the X and Y zeolites, with the rings containing four silicon and two aluminum atoms. As in the case in the crystalline zeolites, it is proposed that two aluminum atoms do not occupy adjoining positions. The order might extend over a sufficient distance to form part of a sodalite cage structure.

Lewis sites such as postulated by Flockhart and Pink (*10*) might indirectly influence the oxidation of perylene if their neutralization reduces the acid strength of closely associated protonic sites. One possible model of such an acid site is given below, and is similar to the model of a protonic site on a decationated zeolite proposed by Uytterhoeven, Christner, and Hall (*34*).


Strong Bronsted acid


Base-exchanged site, weaker Bronsted acid


Base-exchanged and dehydrated

If, as would be expected, both of the Si–OH groups pictured are acidic, this model would explain how ion exchange can decrease acid strength without a decrease in the number of acid sites as well as how one molecule of a nitrogen base could eliminate two strong acid sites. If the arrangement is extended further, possibly to a partly formed sodalite cage structure, it is possible for one molecule of a base to affect the acid strength of several Bronsted sites.

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