

The Measurement of Catalyst Acidity Using Indicators Forming Stable Surface Carbonium Ions*

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Nonaqueous titration using indicators which form stable carbonium ions on the catalyst surface has been applied to the measurement of the acid-strength distribution of acidic solids. These indicators distinguish between the acidity of cracking catalysts and that of aluminas. The acidity measurements correlate much better with catalytic behavior than do the results employing Hammett indicators.

Certain salts of crystalline aluminosilicates are shown to possess acid properties: They stabilize surface carbonium ions and color Hammett indicators. The effect of alkali and alkaline earth ions on a silica-alumina is primarily one of modifying acid strength rather than elimination of acidity. The alkaline earth salts of crystalline and amorphous aluminosilicates have similar acid strength distributions, differing only in degree.

Evidence is presented for the view that Bronsted acidity is responsible for carbonium ion formation and catalytic activity. The nature of the blue species formed on reaction of 1,1-diphenylethylene with silica-alumina is discussed.

INTRODUCTION

Acidic catalysts play a very important role in modern petroleum processing. Catalytic cracking, isomerization, reforming, cationic polymerization, and alkylation are examples of such acid-catalyzed processes; in each case reactions are believed to proceed via a carbonium ion mechanism.

The measurement of the acidity of solid surfaces has been the subject of much research, and a number of different methods have been employed. This literature has been summarized by Holm, Bailey, and Clark (1). Walling (2) suggested measurement of the acid strength of solids by means of indicators; nonaqueous titration of solids employing Hammett indicators has been used to determine not only the amount of acids present, but also the distribution of catalyst acidity in terms of acid strength (3-6).

A recent paper from this laboratory (6) showed that several aspects of catalytic

activity and selectivity could be correlated with the acid-strength distribution as measured by Hammett indicators (Hammett acidity). Despite this, the use of Hammett indicators was shown (6) to have certain limitations. Both cracking catalysts and aluminas possess very strong Hammett acidity, but the acidity of these two types of catalysts differs in a number of important respects. This suggests that at least a portion of the acidity in cracking catalysts is protonic, while alumina contains chiefly Lewis acidity. The color reactions of Hammett indicators on solid catalysts may not be limited to proton transfer reactions as suggested earlier (5).

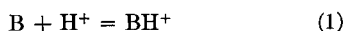
Attention was therefore focused on indicators which might be specific for protonic acids. Diphenylethylene and certain aryl-methanols appeared to be possible indicators of this type. These indicators were also of interest in that the acid form is a carbonium ion. Since many of the acid-catalyzed reactions of interest in petroleum processing are believed to proceed by way of carbonium ion mechanisms, the ability of a catalyst to

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stabilize surface carbonium ions should be related to its catalytic activity. This paper describes the results of acidity measurements on a variety of catalysts employing carbonium ion indicators. The possibility of using arylmethanols as well as Hammett indicators to measure the acid strength of solids was suggested by Walling (2), but no results of such an application have been described.

THEORY

The Hammett H_0 acidity function is based upon the following reaction:

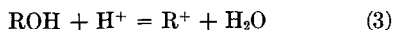


where B is a neutral base and BH^+ is the colored conjugate acid form of the indicator base. The acid strength may be quantitatively expressed by Hammett and Deyrup's H_0 function (7).

$$H_0 = pK_{BH^+} - \log (C_{BH^+}/C_B) \\ = - \log (a_{H^+}f_B/f_{BH^+}) \quad (2)$$

where $pK_{BH^+} = - \log K_{BH^+}$, C_{BH^+}/C_B is the ratio of the concentrations of the indicator in its acid and basic forms, K_{BH^+} is the thermodynamic ionization constant of the conjugate acid BH^+ , a_{H^+} is the hydrogen ion activity, and f_B and f_{BH^+} are activity coefficients.

Arylmethanols, on the other hand, react with strong protonic acids according to the equation (8).



Here the conjugate acid, R^+ , is a colored carbonium ion.

These arylmethanol-carbonium ion equilibria have been used to define a new acidity function (8-10) which has been variously designated as C_0 , J_0 , and H_R . The terminology of Deno *et al.* (10) will be employed here.

$$H_R = pK_{R^+} - \log (C_{R^+}/C_{ROH}) \\ = - \log a_{H^+} + \log a_{H_2O} + \log (f_{R^+}/f_{ROH}) \quad (4)$$

The relationship between the two acidity functions can be obtained by combining Eqs. (2) and (4)

$$H_R = H_0 + \log a_{H_2O} - \log \frac{f_{ROH}f_{BH^+}}{f_Bf_{R^+}} \quad (5)$$

At high acid concentrations ($> 80\%$ H_2SO_4) the last term in Eq. (5) cancels, and the two acidity functions differ by the logarithm of the activity of water. At lower acid concentrations, it was shown by Deno *et al.* (9) that the last term becomes quite significant.

For arylolefin-carbonium ion equilibria, Deno *et al.* (11) derived the expression

$$H_R - \log a_{H_2O} = pK'_{R^+} + \log (C_{ol}/C_{R^+}) \quad (6)$$

The prime was used to distinguish this pK from that for arylmethanol-cation equilibria.

EXPERIMENTAL

Indicators. The indicators used in the present study are listed in Table 1 together with their pK values and the acid concentration at which each is 50% converted to its acid form. The source of these data for the Hammett indicators is given in a previous paper (6); the data for the arylmethanols are, with one exception, taken from Deno, Jaruzelski, and Schriesheim (9). We have redetermined the equilibrium for 4,4',4''-trimethyltriphenylmethanol and found it to be half converted to the carbonium ion at 36% H_2SO_4 rather than 32% as reported (9). The data for 1,1-diphenylethylene is from Deno, Groves, and Saines (11).

The Hammett indicators used were commercial products purified by recrystallization. Diphenyl- and triphenylmethanol were Eastman chemicals purified by recrystallization.

4,4',4''-Trimethoxytriphenylmethanol was prepared by the procedure of Baeyer and Villiger (12) and purified by recrystallization of the picrate and the carbinol. The white crystals melted at 82-82.5° as compared to reported values of 81-82° (9) and 83.5-84° (12).

4,4',4''-Trimethyltriphenylmethanol was prepared by the method of Newman and Deno (13). It melted at 95.8-96.2° (reported 93.4-94.0°).

3,3',3''-Trichlorotriphenylmethanol was prepared as described by Marvel *et al.* (14) and purified by vacuum fractionation, selecting the cut with highest absorptivity in

TABLE I
INDICATORS USED IN ACID STRENGTH DISTRIBUTION MEASUREMENTS

Hammett indicators	pK _a	Acid strength (wt % H ₂ SO ₄)
Butter Yellow	+3.3	3 × 10 ⁻⁴
Dicinnamalacetone	-3.0	48
Chalcone	-5.7	72
Anthraquinone	-8.3	90
Carbonium ion indicators	pK _R ⁺	Acid strength (wt % H ₂ SO ₄)
4,4',4''-Trimethoxytriphenylmethanol	+0.82	1.2
4,4',4''-Trimethyltriphenylmethanol	-4.02	36
Triphenylmethanol	-6.63	50
3,3',3''-Trichlorotriphenylmethanol	-11.03	68
Diphenylmethanol	-13.3	77
4,4',4''-Trinitrotriphenylmethanol	-16.27	88
2,4,6-Trimethylbenzyl alcohol	-17.38	92.5
1,1-Diphenylethylene	—	72

96% H₂SO₄. The product was a light-colored viscous oil which failed to crystallize.

4,4',4''-Trinitrotriphenylmethanol was prepared by the procedure of Fischer (15); it melted at 187°C.

2,4,6-Trimethylbenzyl alcohol was prepared according to Newman and Deno (13). 1,1-Diphenylethylene was obtained from Aldrich Chemical Company and purified by distillation in vacuo.

Titration procedure. Previous to titration, the catalysts were heated to 500°C for 2 hr in a stream of air dried by passage through activated molecular sieves. Titrations were carried out in 3-dram screw-cap vials dried in an oven before use. The catalyst was transferred to the vials as rapidly as possible in a dry box to minimize adsorption of water from the air. Usually, 8–10 vials of each catalyst were weighed out. The desired amount of approximately 0.07 *N* *n*-butylamine in dry benzene was added to each vial. Usually, the amount of *n*-butylamine added to successive vials varied in increments of 0.015 meq/g. The vials were shaken vigorously several times and allowed to equilibrate overnight in a desiccator.

The extent of neutralization was determined by placing benzene solutions of the appropriate indicators in oven-dried 1-dram screw-cap vials and transferring a small amount of equilibrated catalyst to the vial. After allowing about 5–15 min (as needed)

for reaction of the indicator, the catalyst in the tightly closed vial was examined with a 40-power hand microscope. The endpoint is that point at which only a few particles remain which have the acid-color of the indicator.

If required, additional amounts of *n*-butylamine were added to the vials, and the above procedure repeated.

In the case of Hammett indicators, 0.01% solutions were used, while 2 g/liter solutions of the carbonium ion indicators are now employed. Some of the results herein were obtained with 0.2 g/liter solutions before it was found that with some catalysts and indicators the higher concentration is needed.

All benzene used as solvent was dried by percolation through freshly activated molecular sieves. This treatment reduces the water content to below 10 ppm.

Catalysts. The cracking catalysts and aluminas were the same as those previously described (6). The 13X and 10X molecular sieves were purchased from the Linde Co. In most cases, the ion-exchanged M-46 (6) and 13X catalysts were prepared by three exchanges with 1 *N* solutions of the corresponding acetates or chlorides, followed by washing with distilled water. The barium- and potassium-exchanged M-46 were prepared by a single soaking in the corresponding acetates for several days.

Mallinckrodt silicic acid, designated "for

chromatographic purposes according to the procedure of Ramsey and Patterson" was employed in the preparation of mounted acids.

The fluorided F-10 alumina was prepared by treatment with aqueous HF followed by calcination at 500°C and contained 3.15% fluorine by analysis.

RESULTS AND DISCUSSION

Titration of Mounted Acids

Silicic acid, a form of silica gel with large pores, was added to dilute sulfuric acid to form a thick slurry. This product was dried overnight at 120° and titrated with *n*-butylamine with the results given in Table 2.

TABLE 2
ACIDITY DISTRIBUTION OF H_2SO_4 MOUNTED
ON SILICIC ACID (1.81 MEQ/G)

H_R indicators		Hammett indicators	
Wt % H_2SO_4	<i>n</i> -Butylamine titer ^a	Wt % H_2SO_4	<i>n</i> -Butylamine titer ^a
1.2	1.43	3×10^{-4}	1.43
36	1.43	48	1.43
50	1.43	72	1.37
68	1.37	90	0.37
77	1.30		

^a *n*-Butylamine titer, Meq/g stronger than designated H_2SO_4 concentration.

The Hammett and arylmethanol indicators define a single curve within experimental error when the titer is plotted against acid strength. Nearly all of the acid sites are stronger than 70% H_2SO_4 , but only about 25% exceed 90% acid strength. The total acidity found was less than added initially.

Since aqueous titration with KOH using phenolphthalein as indicator gives the same value for total acidity, it is concluded that some of the H_2SO_4 was volatilized.

Heating the mounted H_2SO_4 to 250° for 2 hr reduced the total acidity to 1.35 meq/g but 60% of the acid sites were now stronger than 90% H_2SO_4 .

Perchloric acid was mounted on silicic acid in a similar manner and dried at 120°. Titration gave results similar to the above except that in this case only 15% of the acid sites were stronger than 90% H_2SO_4 . In titrating acids mounted on silica gel, Benesi (4) also found that the acidity stronger than 90% H_2SO_4 was a small part of the total acidity, and advanced two possible explanations for this result. The marked increase in the amount of strong acidity upon raising the drying temperature suggests that the acid strength of mounted acids is reduced by adsorbed water in a manner analogous to the effect of adsorbed water on reducing the acid strength of solid acids (6).

Acidity Distributions of Commercial Cracking Catalysts

Data for four catalysts are given in Table 3. The kaolin-derived catalyst has the largest proportion of strong (> 77% H_2SO_4) acid sites. The high-alumina (25% alumina) synthetic catalyst and the silica-magnesia catalyst have similar acid strength distributions with a relatively high proportion of intermediate strength and weak acidity. Hammett acidities of three of these catalysts were given in a previous paper (6) and the acid strength distributions were generally similar to those in Table 3. The two acidity

TABLE 3
ACIDITY DISTRIBUTIONS OF COMMERCIAL CRACKING CATALYSTS USING H_R INDICATORS

Catalyst acid strength (wt. % H_2SO_4)	<i>n</i> -Butylamine titer, meq/g stronger than designated H_2SO_4 concentration			
	Silica-magnesia	Silica-alumina (25% alumina)	Halloysite	Kaolin
1.2	0.60	0.50	0.165	0.125
36	0.43	0.38	0.105	0.115
50	0.38	0.30	0.075	0.105
68	0.33	0.30	—	—
77	0.28	0.27	0.075	0.085
88	>0	>0	0	>0

distributions differ appreciably for the high-alumina catalyst, which has only 0.30 meq/g of acidity at $pK + 3.3$ and $pK - 3.0$. The Hammett indicators show no acidity weaker than 50% H_2SO_4 compared to 0.20 meq/g using H_R indicators.

A 2 g/liter solution of 4,4',4''-trinitrotriphenylmethanol was found to give a strong yellow coloration to the high-alumina synthetic catalyst, a pale yellow to the kaolin-derived and silica-magnesia, and no observable color to the halloysite-derived catalyst. Quantitative data are not available because a 0.2 g/liter solution of the indicator employed at the time failed to give the acid color. All of these catalysts are strongly colored by a 0.05 g/liter solution of triphenylmethanol. The equilibrium constant for the arylmethanol-carbonium ion equilibrium appears to be a function of the stability of the carbonium ion.

2,4,6-Trimethylbenzyl alcohol was found to produce a pale pink to light purple color with cracking catalysts rather than the yellow color characteristic of the carbonium ion. For this reason, it may not be suitable for measuring the acid strength of solids.

Effect of Alkali and Alkaline Earth Ions on H_0 and H_R Acidity of Silica Alumina

The effect of ion exchange with alkali and alkaline earth acetates on the acidity of

M-46 silica-alumina cracking catalyst is shown in Table 4. For M-46 itself, the titers obtained with H_0 and H_R indicators differ rather little between 30–90% H_2SO_4 . The amount of acidity weaker than 30% H_2SO_4 is considerably greater with H_R indicators than with H_0 indicators.

Ion exchange greatly increases the difference in titer obtained with the two classes of indicators. The potassium-poisoned catalyst has no H_R acidity as strong as 77% H_2SO_4 , but still has about half the original H_0 acidity stronger than 90% H_2SO_4 .

The reduction in strong (> 77% H_2SO_4) H_R acidity increases with the size of the ion within a given group of the periodic table. Calcium has less effect than barium, and lithium much less effect than potassium. This is in accord with the results of Danforth (16), who found that the poisoning effect of alkali metal ions on cracking activity increased with the ion size.

Known amounts of KOH were added to M-46 in aqueous suspension; after drying and calcining at 500°, the catalysts were titrated, with the results shown in Table 5. The total acidity of M-46 initially is about 0.35 meq/g; the addition of that quantity of KOH does not neutralize all of the acidity; in fact, only about 1/3 of the total acidity disappears along with about half of the strong acidity. Adding 0.60 meq/g destroys

TABLE 4
EFFECT OF ION EXCHANGE ON ACIDITY DISTRIBUTION OF M-46

Acid strength (wt % H_2SO_4)	<i>n</i> -Butylamine titer, meq/g stronger than designated H_2SO_4 concentration				
	M-46 ^a	M-46 + Ba	M-46 + Ca	M-46 + K	M-46 + Li
<i>H_R Indicators</i>					
1.2	0.35	0.23	0.28	0.19	0.26
36	0.24	0.17	0.19	0.13	0.18
50	0.22	0.17	0.16	0.11	0.18
68	0.20	0.12	0.14	—	—
77	0.195	0.11	0.14	0	0.11
88	0.19	>0	>0	0	0
<i>H₀ Indicators</i>					
3×10^{-4}	0.22	0.19	0.18	0.16	0.23
48	0.21	0.19	0.18	0.16	0.23
90	0.20	0.14	0.15	0.09	0.20

^a The M-46 was hydrated by soaking in distilled water 3 days before activation in order to be more comparable to the ion-exchanged samples which may be partially rehydrated during exchange.

TABLE 5
EFFECT OF AQUEOUS KOH ON ACIDITY OF
M-46 SILICA-ALUMINA (H_R INDICATORS)

Acid strength (wt % H_2SO_4)	<i>n</i> -Butylamine titer, meq/g stronger than designated H_2SO_4 concentration		
	M-46	M-46 plus 0.35 meq/g KOH	M-46 plus 0.60 meq/g KOH
1.2	0.31	0.22	0.18
36	0.21	0.135	0.09
50	0.205	0.12	0.09
77	0.18	0.075	0.0

all of the strong acidity, but half of the original acidity remains. A progressive reduction in acid strength results as more alkali is added.

The results above make it clear that the effect of adding metal ions to silica-alumina is not simply replacement of protons by metal cations with complete neutralization and disappearance of acid sites. Rather, the effect appears to be a modification of acid strength distribution in which strong acid sites are eliminated, and replaced in some manner, little understood at present, with sites of less acid strength. The results of neutralization with aqueous KOH are certainly in part due to the fact that as the original acid sites are neutralized, new acid sites are created by rehydration of the catalyst catalyzed by hydroxyl ions.

Benesi (5) showed that montmorillonite and kaolinite clays completely exchanged with sodium or ammonium ions and dried at 120° surprisingly possessed acidity stronger than 48% H_2SO_4 . He proposed that all exchange positions cannot be occupied because of steric hindrance (or electrostatic repulsion) between the highly solvated cations. Upon drying, the solvation shell surrounding each cation is removed, thereby exposing other acidic exchange positions. Such a picture would imply that ion exchange of the hydrogen form with alkali cations should reduce the number of sites, but that the acid strength distribution of the remaining sites should be similar to that initially present in the hydrogen form, unless the alkali cations can interact with neighboring protons to effectively reduce the acid strength.

It has been found that the cumene-cracking activity of ion-exchanged silica-alumina

catalysts at 440°C correlates better with the H_R acidity measurements than with H_0 values (17). The activities vs. H_R acidity stronger than 77% H_2SO_4 fall along a straight line through the origin. There is reason to believe activity would correlate better with H_R acidity stronger than 88% H_2SO_4 , but sufficient acidity data at this level are not available. A plot of activity vs. strong Hammett acidity defines a straight line which does not approach the origin since the potassium-exchanged M-46 has no activity while appearing to have 0.09 meq/g of acidity at $H_0 = -8.3$.

The Acidity of Crystalline Aluminosilicates

It has recently been reported that certain crystalline aluminosilicates (molecular sieves) are able to catalyze cracking (18) and isomerization (19) reactions, which have hitherto been ascribed to acidity. Replacement of the sodium ions in Linde 13X molecular sieve (a synthetic faujasite) with calcium ions leads to a material, designated as 10X, with greatly increased catalytic activity. It is active for cumene cracking whereas the 13X sieve is not (18). Both groups of workers have indicated that concepts other than acidity are needed to explain the catalytic behavior of molecular sieves, because of the well-known fact that alkali and alkaline-earth metals poison the cracking activity of silica-alumina (20). Rabo *et al.* (19) have postulated that the activity is due to an intense Coulomb field resulting from asymmetric placement of the divalent calcium ion between two ion exchange positions.

Data on the titration of 13X zeolite (obtained as a powder), and 13X exchanged with lithium and calcium ions are summarized in Table 6. The 13X itself gave no coloration with any of the H_R indicators but developed a red color with butter yellow, but not with benzene-azodiphenylamine ($pK_a = +1.4$). Both the Li-X and Ca-X zeolites gave the characteristic yellow color of the trityl ion when treated with triphenylmethanol. The data for Li-X indicate that a divalent ion is not a requirement for development of acidity (19), although the amount developed is small. The cumene-

TABLE 6
ACIDITY DISTRIBUTIONS OF SALTS OF X ZEOLITE

Acid strength (wt % H ₂ SO ₄)	<i>n</i> -Butylamine titer, meq/g stronger than designated H ₂ SO ₄ concentration		
	13X (Na-X)	Ca-X	Li-X
	<i>H_R Indicators</i>		
1.2	0	0.50	.08
36	0	0.29	.04
50	0	0.17	.02
68	0	0	0
	<i>H₀ Indicators</i>		
3 × 10 ⁻⁴	0.32	0.35	0.04
48	0	0.26	0.03
72	0	0.03	0

cracking activities were found to be proportional to the measured H_R titration values (17).

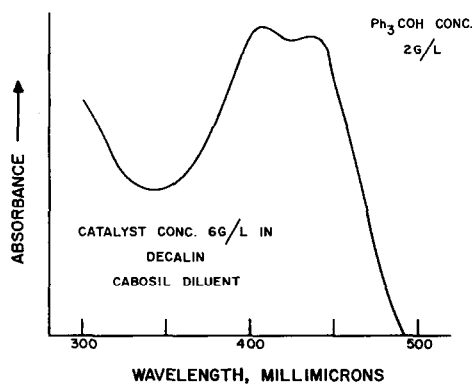


FIG. 1. Trityl ion chemisorbed on Ca-X zeolite.

Figure 1 shows the spectrum of the trityl ion adsorbed on the surface of the calcium X zeolite. It was obtained by suspending a mixture of the zeolite and Cabosil in a solution of triphenylmethanol in decalin (21). The Cabosil serves the double purpose of keeping the catalyst uniformly suspended and as an inert diluent. The spectrum is typical of the triphenylcarbonium ion and closely resembles the spectrum of this ion adsorbed on a silica-alumina catalyst (22, 23). This spectrum, and similar ones obtained on other zeolite salts, is positive evidence that the colorations obtained with H_R indicators are due to surface carbonium ions.

The concentration of the triphenylcarbonium ion on the calcium X zeolite was calculated to be 1.2×10^{-6} moles/g (21), considerably less than the $2-2.9 \times 10^{-5}$ moles/g reported by Leftin and Hall (23a) for the surface of Houdry M-46 catalyst. This low figure undoubtedly does not indicate the number of sites capable of generating trityl ions. Most of these sites are in the interior cavities of the crystal and the 10Å openings exclude the triphenylmethanol molecule, whose diameter is about 14Å.

These synthetic zeolites are available from Linde both as powders and as pellets. The latter contain 20% of clay binder (24). Table 7 compares acidity measurements

TABLE 7
ACIDITY OF PELLETED AND POWDERED 13X AND 10X ZEOLITES

Acid strength (wt % H ₂ SO ₄)	<i>n</i> -Butylamine titer, meq/g stronger than designated H ₂ SO ₄ concentration			
	Linde 13X		Linde 10X	
	Pellets	Powder	Pellets	Powder
	<i>H_R Indicators</i>			
1.2	0.32	0	0.57	0.19
36	0.13	0	0.22	0.05
50	0.07	0	0.11	0.01
68	0	0	0.01	0
77	—	—	0.01	0
	<i>H₀ Indicators</i>			
3 × 10 ⁻⁴	0.53	0.35	0.17	0.05
48	0.10	0	0.11	0.04
72	0	—	0.01	0
90	—	—	0	0

made on 13X and 10X zeolites in pellet and powder form. It is clear from these data that the clay binder used is not inert, but possesses a considerable amount of acidity.

Subsequent to the completion of the work described above, it was reported elsewhere (25) that molecular sieves are acidic toward Hammett indicators. All of the work described, however, was performed on the pelleted sieves. The present data for the first time demonstrate inherent acidic behavior in the pure zeolites. Much of the olefin-polymerization activity reported (25) may also have been catalyzed by the clay binder.

We have seen above that when silica-alumina is ion-exchanged to saturation with calcium ion it does not, by any means, lose all of its acidity; the curve of acidity versus acid strength becomes much more steep because of the preferential loss of a considerable fraction of the strong acidity. [The addition of sufficient $\text{Ca}(\text{OH})_2$ could perhaps destroy most or all of the acidity.] The acid-strength distribution curves of the Ca-M-46 and the Ca-X sieve are somewhat similar except that the former appears to have stronger acid sites. The crystalline and amorphous aluminosilicates appear to differ in degree, rather than in kind. In both cases, the alkaline earth salts are more acidic than the alkali metal salts. We believe that the evidence justifies a conclusion that certain crystalline aluminosilicates are acidic, and that this acidity is responsible for many of their catalytic reactions, at least in those instances where the products are characteristic of carbonium ion reactions. The nature of the acid sites responsible is far from clear. (See Note Added in Proof, at end of paper.)

Not all activity of molecular sieves, however, appears to be due to acidity. The 13X zeolite was found to be active for the cracking of decane (18) in spite of the apparent absence of all but very weak acidity. The nature of the products in this case suggests cracking by a free radical rather than a carbonium ion mechanism. No branched molecules were found in the products (18). The gaseous products are rich in C_1 and C_2 rather than C_3 and C_4 hydrocarbons (17).

Acidity of Some Aluminas

F-1 alumina, washed with acetic acid to remove sodium, was found not to give a coloration with any of the H_R indicators. F-10 alumina, which contains 0.5% chloride, was acid toward $\text{p}K_{R^+}$ +0.82 and -4.2 indicators, but not toward triphenylmethanol. The results of acidity titrations on F-10 alumina, and F-10 alumina treated with HF (calcined at 500°) are given in Fig. 2. Treatment with HF is seen to have greatly increased the acid strength using H_R indicators. After HF treatment, the product gave a coloration with 1,1-diphenylethylene (DPE) whereas F-10 does not. The titer using

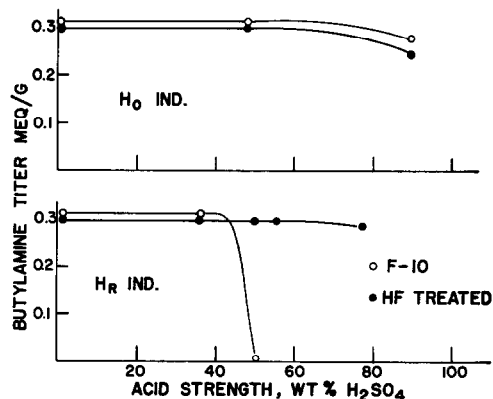


FIG. 2. Effect of HF on acidity of F-10 alumina.

DPE as indicator was 0.17 meq/g, appreciably lower than with the other indicators.

Weber has shown that fluorided alumina and silica-alumina bases impregnated with platinum salts have high hydrocracking activity, whereas on a chlorided alumina the hydrocracking activity is low (26). Webb (27), on the basis of the effect of temperature on ammonia chemisorption, concluded that HF treatment of alumina did not increase the number of acid sites, but did considerably increase their strength. Holm and Clark (28) report that fluoriding alumina considerably increases its activity for *n*-octane cracking, *o*-xylene isomerization, and propylene polymerization. The data with H_R indicators are clearly in far better accord with these properties of HF-treated alumina than those with H_0 indicators, which would predict little difference in properties. The results suggest that strong H_R acidity is needed for high cracking activity. These data also suggest that diphenylethylene and H_R indicators measure the same type of acidity.

Eta alumina, produced by the dehydration of β -alumina trihydrate, was found to give an acid coloration with triphenylmethanol, but not with 3,3',3''-trichlorotriphenylmethanol or DPE.

Thus, the absence of very strong H_R acidity differentiates alumina from cracking catalysts. However, a 2 g/liter concentration of indicator is required for a color comparable to that obtained with an 0.05

g/liter solution applied to M-46; the equilibrium constant for conversion to the carbonium ion is apparently much smaller on alumina than on silica-alumina.

Based on the finding that fluorided alumina, and silica-alumina catalysts containing 10 to 45% alumina, have lower heats of ammonia adsorption than pure alumina at high coverages, it was concluded by Clark *et al.* (28) that fluoriding reduces the acid strength of alumina and that typical acid-catalyzed hydrocarbon conversion reactions such as cracking, isomerization, etc., occur most readily on relatively weak acid sites. This conclusion assumes that the heat of ammonia adsorption is a single-valued measure of acid "strength" even when two distinctly different types of acidity, Lewis and protonic, may both be present. The validity of this assumption is questionable, for the relative strengths of even Lewis acids depend upon the particular base used for reference (5), and it is contradicted by the observations with arylmethanol indicators, and the results of Webb (27). If it is postulated that a strong protonic acid may have a lower heat of ammonia adsorption than certain Lewis acids, the data of Clark (28) are consistent with our view that strong H_R (probably protonic) acidity is responsible for catalytic activity.

Diphenylethylene as an Indicator

When 1,1-diphenylethylene (DPE) reacts with a silica-alumina catalyst, it forms the yellow methyl-diphenylcarbonium ion and in addition a second species with an absorption band at 605 $m\mu$ which, in the absence of the carbonium ion, has a blue color. The presence of both species imparts a green color.

The nature of this blue species has been the subject of some dispute and has not been definitely established (22, 23b, 30, 31 and references cited therein). It has been postulated that it is an aromatic radical ion (23b, 31, 32). Very recently, Rooney and Pink (34) have shown by the addition of water that the blue species is diamagnetic, and propose that it is formed on hydration from a radical ion. This suggestion appears

inconsistent with the observation (30b, 31b) that addition of water does not increase the absorption at 605 $m\mu$, as well as with other observations noted below. We have found, however, that the blue species can be desorbed from the catalyst in substantially colorless form by organic bases such as alcohol or acetone and that the material so obtained behaves as an acid-base indicator (21). It is instantly reconverted to its blue color by strong acids and decolorized upon reducing the acidity of the medium. These observations are more consistent with a hypothesis that it is a blue carbonium ion of unknown structure, possibly derived from a trimeric reaction product of DFE, rather than a radical ion. Cookson, Rosenbaum, and Symons have shown that a blue carbonium ion is formed from the reaction product of 1,1-di(*p*-methoxyphenyl)ethylene and formic acid (33). Leftin and Hall (31b) have stated that their observations are consistent with the hypothesis that the blue species arises from reaction of a methyl-diphenylcarbonium ion with a molecule of 1,1-diphenylethylene. Our own observations have led us to this same conclusion (21).

When DPE is used as an indicator in an acidity titration, it is found that above a certain quantity of *n*-butylamine, the catalyst no longer develops any green-colored particles after allowing DPE and catalyst to react for several hours. Long before this point in the titration is reached, the catalyst ceases to give an observable yellow coloration, apparently because the color of the methyl-diphenylcarbonium ion is relatively weak compared to the triaryl carbonium ions. Thus, the only readily observable endpoint is that due to the blue species, rather than to the methyl-diphenylcarbonium ion itself.

If a methyl-diphenylcarbonium ion is an intermediate in the formation of the blue species, the surface acid strength at the DPE endpoint should be substantially the same as that required to form this ion from DPE, namely, 72% H_2SO_4 (11), regardless of the pK value corresponding to the equilibrium between the blue species and its conjugate base (which appears to be in the vicinity of 50% H_2SO_4). Use of the conjugate base of the blue species as an

indicator in catalyst titration gives a different endpoint from DPE itself.

DPE has been used as an indicator in the titration of many catalysts with butylamine. Those catalysts insufficiently acidic to give coloration with H_R indicators corresponding to 68% or 77% H_2SO_4 do not give a coloration with DPE. Those which are sufficiently acidic to color these H_R indicators usually are colored by DPE, although there are a few exceptions to this rule as in the case of some alkali-poisoned catalysts. When the butylamine titers using arylmethanol indicators are plotted vs. acid strength, the data for DPE (plotted at 72% H_2SO_4) in many instances falls close to or slightly below the line. (This can be construed as evidence that the carbonium ion is involved in formation of the blue species.) There appears to be no correlation between strong Hammett acidity and the DPE color reaction. Therefore, it appears that the arylmethanols and DPE are measuring the same type of acidity; if protonic acidity is responsible for the DPE color reaction it is also responsible for the color reactions of the H_R indicators.

If the surface carbonium ions are formed from arylmethanols according to Eq. (3), the extent of the reaction will be influenced by the activity of water on the catalyst surface as well as by the proton-donating tendency of the catalyst. This is, of course, equally true in the case of aqueous acids. However, catalytic solids may differ appreciably in water affinity, and it may, therefore, appear preferable to define the acidity of solids by Eq. (6), where $H_R - \log a_{H_2O}$ would define a new acidity function H'_R (11). We have looked at several olefins which would be possible indicators for defining such a function, in addition to DPE, but due to instability or side reactions with the catalyst they did not appear to be suitable indicators. A series of substituted 1,1-diphenylethylenes might be suitable for this purpose.

The Nature of the Acid Sites

The nature of the active acid centers on a cracking catalyst has been a matter of dispute for some years; references to the pertinent literature have been reviewed elsewhere (6). Strong protonic acids on the

catalyst surface would convert arylmethanols to the corresponding cation according to Eq. (3); proponents of Lewis acidity might prefer to visualize the reaction as abstraction of a hydroxide ion by a Lewis acid. According to either interpretation, one would expect that the more unstable the carbonium ion, the stronger the acidity which would be required to stabilize the carbonium ion on the surface.

Webb (27) concluded from infrared observations that both fluorided and non-fluorided alumina were Lewis acids, because in neither case were ammonium ions detected; Clark *et al.* (28) concluded from heats of ammonia chemisorption that the acid sites on fluorided alumina were weaker than on alumina. Since fluorided alumina has much stronger acidity than alumina on the basis of its reaction with arylmethanol indicators, both of the above conclusions cannot be correct. If the first conclusion is correct, one would, however, expect that the heat of ammonia adsorption would indicate the relative strength of the two Lewis acids. The observations with arylmethanol indicators and the heats of ammonia adsorption can be reconciled if it is assumed that the acid centers on fluorided alumina are of a different type (e.g. protonic) from those on alumina. The facts that fluorided alumina converts 1,1-diphenylethylene to the carbonium ion and that it shows no increase in acid strength with Hammett indicators support this assumption, from which follows the conclusion that protonic acids rather than Lewis acids convert arylmethanols to their corresponding cations.

The fact that data for arylmethanols and 1,1-diphenylethylene fall along the same curve, when butylamine titers of silica-alumina are plotted vs. the acid strength (wt % H_2SO_4) required to protonate the indicators to generate the corresponding ions, is also evidence for generation of the carbonium ions by Bronsted rather than Lewis sites. Generation of the carbonium ion from DPE is easier to explain on the basis of proton addition, although generation by reaction with Lewis acids has been postulated (30a). If Lewis acids react with both DPE and arylmethanols to generate the carbonium ions, one would not expect

DPE to fall on the same curve with the arylmethanols, for the acid strengths employed relate to the relative ease of *protonation*. The relative ease of reaction of DPE with Lewis acids, as compared to a series of arylmethanols, would not be expected to be the same as observed in the protonation reaction, particularly since an Al-C bond would be formed in one case and an Al-O bond in the other.

Additional arguments for the reaction of arylmethanols with protonic catalyst sites are discussed in another communication (35), wherein it is shown that the chemisorption of triphenylmethane and perylene on silica alumina are not good evidence for strong Lewis sites, as is widely believed (23, 32, 34, 36), but rather are indicative of Bronsted sites.

Regardless of interpretations as to the type of acid sites responsible, it appears that titrations using H_R and H'_R indicators will prove valuable in defining an important chemical property of solid surfaces, and lead to useful correlations with catalytic activity. Since eta alumina has been found to stabilize certain carbonium ions, while acid-washed F-1 alumina does not, it is believed H_R indicators can distinguish between the "intrinsically acid" and nonacid types of alumina described by Pines and Haag (37) and thus correlate with their catalytic behavior.

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NOTE ADDED IN PROOF

A possible explanation for the acidity of the cationic aluminosilicates is that the polarizing action of the field of the cation tends to free (make acidic) a proton of a hydroxyl group attached to an adjacent silicon or aluminum atom, or a proton of a water molecule adsorbed on the cation itself. Bertsch and Habgood [*J. Phys. Chem.* **67**, 1621 (1963)] find that water is adsorbed on LiX and NaX zeolites simultaneously by an ion-dipole interaction

with the cation and by hydrogen bonding of one of the hydrogens to an oxygen atom of the zeolite surface. The greater the field strength of the cation, the stronger would be the resultant acidity. Thus, the acid strength should increase with increasing charge and decreasing size of the cation, as has generally been observed (refs. 17, 19, and Tables 4 and 6). Asymmetric placement of a divalent ion between two ion exchange positions as proposed by Rabo (19) would intensify the field of the cation. Weyl [Weyl, W. A., and Marboe, E. C., "Constitution of Glasses," p. 56. Interscience, New York, 1962] has suggested that acidity is linked to the field strength of the cation.

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