Acid Strength Distribution Studies of Catalyst Surfaces

ALFRED E. HIRSCHLER and A. SCHNEIDER
Sun Oil Co., Marcus Hook, Pa.

A CONSIDERABLE amount of research on the measurement of the acidity of solid surfaces and the correlation of acidity tests with catalytic activity has been stimulated by the importance of acid-type catalysts in petroleum processing. This literature has recently been summarized by Holm, Bailey, and Clark (*7*).

The nonaqueous butylamine titration procedure described by Johnson (*8*) appeared to be an attractive method for catalyst acidity measurement, and suggested to us that the acid-strength distribution of a catalyst surface could be obtained by titration using a series of Hammett indicators. Work along these lines was initiated in 1956, and this article summarizes some of the results of these acid-strength distribution measurements. The results of a few measurements of this type have already been described independently by Benesi (*3*). The relation between catalytic activity and acid-strength measurements will be considered.

EXPERIMENTAL

Indicators. The Hammett indicators used in the present study are listed in Table I and ranged in basicity from *p*-ethoxychrysoidin ($pK_a = +5.0$) to anthraquinone ($pK_a = -8.3$). 2,4,5-Trinitroaniline ($pK_a = -9.4$) was found unsuitable for indicating the acid strength of solids because it gives colored reaction products with nonacidic solids.

Table I. Indicators Used in Acid Strength Distribution Measurements

Indicator	pK_a	Acid Color
p-Ethoxychrysoidin	+5.0[a]	Red
Butter yellow	+3.3[b]	Red
Benzeneazodiphenylamine	+1.4[c]	Purple
4-Dimethylaminoazo-1-naphthalene	+1.2[a]	Purple
Dicinnamalacetone	−3.0[b]	Red
Chalcone	−5.7[c]	Yellow
Anthraquinone	−8.3[c]	Yellow

[a] Johnson (*8*).
[b] Benesi (*1*).
[c] "Best values" selected by Paul and Long (*12*).

With one exception, the indicators employed are the same as those used by Benesi (*1*), who has shown that this class of indicators can be used to estimate the acid strength of solid surfaces in terms of Hammett and Deyrup's (*5*) H_0 scale.

The indicators used were commercial products purified by recrystallization.

Titration Procedure. Titrations are carried out in 3-dram screw-cap vials which are kept in an oven at 120° C. These are removed from the oven, capped tightly, and allowed to cool about 10 minutes before being weighed on an analytical balance. Roughly 0.5 to 1 gram of calcined catalyst (depending on the acidity level) is rapidly transferred to each vial using a calibrated scoop and funnel, and the vial is quickly recapped and weighed. The catalyst is covered with dry benzene and the desired amount of standard *n*-butylamine in benzene is added (approximately 0.07*N*) by using a 1-ml. pipet, graduated in 0.01 ml., mounted on a stand and controlled by a Volumette hand pipet. If more than 2 ml. is required, the first addition is made with a standard volumetric pipet to the nearest milliliter.

Usually three to six vials of each catalyst are weighed out. The amount of butylamine added to the several vials may differ in steps of about 0.02 to 0.10 meq. per gram depending on the expected level of acidity. The vials are shaken vigorously and allowed to equilibrate for at least 2 or 3 hours, the time increasing to overnight as the end point is approached.

After equilibration, the extent of neutralization is determined, beginning with the vial containing the most titrant. Except for anthraquinone and chalcone, which have weakly colored (yellow) conjugate acids, the following procedure is used. A small amount of catalyst is removed and placed in a 1-dram screw-cap vial containing a 0.01% benzene solution of the indicator, and the vial is capped. After allowing a few minutes for diffusion and reaction of the indicator, the vial is carefully inverted so that the catalyst remains at the bottom and the catalyst is examined using a 40-power hand microscope. The state of neutralization can be tested with any desired number of indicators, testing first for the strongest acids.

The titration is continued in this manner until the sample is neutralized to all indicators of interest, maintaining stepwise differences of 0.01 to 0.10 meq. per gram between different samples of catalyst. The steps are narrowed as the end point is approached. The 3-dram vials are kept tightly closed in a desiccator, except when additions are being made.

The procedure for chalcone and anthraquinone is similar, except that when the end point is approached, indicator is added to the 3-dram vials of catalyst, and the end point is determined by comparing several vials with differing amounts of titrant. For this purpose, the vials are carefully inverted and the color of the larger particles of catalyst at the bottom of the vial are examined through the flat bottom of the vial.

Colored catalysts are titrated by adding 0.15 to 0.3 gram of a white catalyst of known acidity (*8*), ground to 100 to 120-mesh, to 0.5 to 1 gram of −200-mesh unknown. The procedure used is similar to that described above for chalcone; the larger particles of the indicator catalyst settle to the bottom of the vial and can be observed through the bottom of the vial without too much masking from the colored catalyst. Microscopic observation improves the sensitivity of the end point. The titer of the indicator catalyst is substracted from the volume of titrant added to the mixture in calculating the acidity of the unknown. It is assumed that both catalysts simultaneously reach the end point at a given H_0 level. The validity of this procedure was confirmed with mixtures of two noncolored catalysts which had been separately titrated.

Catalysts. The chrome bead catalyst (Socony-Mobil Oil Co.) is a synthetic silica-alumina catalyst containing about 11% of alumina and 0.5% of chromic oxide. The M-46 and S-34 (Houdry Process Corp.) are synthetic silica-alumina catalysts containing 11% of alumina. Montmorillonite and halloysite clay cracking catalysts (Filtrol Corp.) were designated as grades 62 and 63, respectively. The composition of grade 62 is 16% alumina, 74% silica, 5% magnesia, 3% CaO; that of grade 63 is 43% alumina and 57% silica. The kaolin was a commercial catalyst developed by the

Houdry Process Corp. and manufactured by International Minerals and Chemical Co.; its composition is 44% alumina, 54% silica, and 1.7% titania. The high alumina catalyst (Davison Chemical Co. No. 55-280 Fluid silica-alumina grade C-1-25) contained 25% of alumina. The silica–magnesia catalyst (Davison Type DA-5) was designated TS-55-3084 and contained 32% of magnesia and 67% of silica. The F-1 and F-10 aluminas (Aluminum Co. of America) contained 0.8% of sodium, and 0.5% of chloride respectively.

Preparative details for some of the modified silica-alumina catalysts listed in Table II are as follows. The code number is the same as that given in column 2, Table II:

CATALYST 4. Dried M-46 pellets were treated with enough ammonium dichromate solution to wet the catalyst, dried, and heated to 732° C. to convert the dichromate to chromium trioxide before steam aging.

CATALYST 5. Fresh Socony chrome bead catalyst was placed in a copper pipe. Anhydrous hydrofluoric acid diluted with nitrogen was passed upward through the catalyst bed for 16 hours. After drying at 130° C., the catalyst contained 6.2 weight % of fluorine.

CATALYST 6. Catalyst 5 was used to crack long range gas oil at 510° C., liquid hourly space velocity (LHSV) of 1 *V/V* per hour; 20-minute process period in a bench scale fixed bed reactor for 25 cycles of use and regeneration. Analysis showed 3.4% of fluorine.

CATALYST 7. Chrome bead catalyst was wet with absolute ethyl alcohol and soaked overnight in a 16% solution of 48% aqueous HF in absolute ethyl alcohol (7.5 grams of HF per 100 grams of catalyst). After draining, the beads were immersed in an ethyl alcohol solution containing 9.2 grams of chromium nitrate per 100 grams of catalyst for 4 days. The beads were dried at 110° C. and calcined 1.5 hours at 706° C. Analysis: 0.9% Cr_2O_3.

CATALYST 8. M-46 pellets were soaked for 3 days in a solution containing 16% by weight of 53.5% aqueous HF in absolute ethyl alcohol, using 7.5 grams of HF per 100 grams of catalyst. The drained pellets were soaked 4 days in alcoholic $Cr(NO_3)_3 \cdot 9H_2O$ (36 grams per 100 grams of catalyst), dried at 121° C., and calcined 1.45 hours at 706° C. Analysis: 5.1% Cr_2O_3, 3.7% fluorine.

CATALYST 9. Dried chrome bead catalyst was wet with absolute ethyl alcohol, drained, and soaked overnight in a 24% solution of 48% aqueous HF in absolute ethyl alcohol (7.5 grams of HF per 100 grams of catalyst). The beads were dried, then calcined 2 hours at 567° C. Analysis: 4.9% fluorine.

CATALYST 10. Dried chrome beads were soaked in an alcoholic solution containing 10% of 48% aqueous HF and 10% of 85% orthophosphoric acid (6.7 grams of HF and 12 grams of H_3PO_4 per 100 grams of catalyst) for 16 hours, then dried and calcined at 538° C.

CATALYST 11. Dried chrome bead catalyst was wet with absolute ethyl alcohol and soaked overnight in a solution containing 6.2% by weight of 48% aqueous HF in ethyl alcohol (7.5 grams of HF per 100 grams). The drained beads were soaked 4 days in an 18% solution of $Cr(NO_3)_3 \cdot 9H_2O$ in absolute ethyl alcohol (9.2 grams of chromium nitrate per 100 grams of catalyst). The beads were dried and calcined at 706° C.

Nitrogen surface areas of some of the catalysts of Table II were determined by a modification of the procedure of Nelsen and Eggertsen (*11*).

Before titration, catalysts were ground to through 100- or 200-mesh and dried by heating to 500° C. for 2 or 3 hours in a muffle furnace. The hot catalyst was removed from the muffle, poured quickly into a 2-ounce wide-mouthed, screw-cap bottle (preheated to 120° C. in an oven). The bottle was capped tightly and was immediately placed in a desiccator over activated Linde 5A Molecular Sieves.

RESULTS AND DISCUSSION

Acidity Distributions of Cracking Catalysts. The *n*-butylamine titers plotted as a function of acid strength are shown in Figure 1 for an M-46 synthetic silica-alumina catalyst both new and steam-aged (732° C. for 4 hours in 100% steam). These titers are cumulative—i.e., they are measures of the number of acid centers in milliequivalents per gram having an H_0 equal to or lower than the pK_a value of the indicator used. The actual amount of surface acid in a given H_0 range is given by the difference in titer using the two indicators bracketing that H_0 range.

The new silica-alumina catalyst appears to have a continuous distribution of acid strengths, although most of the acidity is very strong. The indicators behave in a consistent manner, as shown by the fact that the points lie on a smooth curve. Steam aging results in a loss of acidity at all acid strength levels, but the loss is most marked for the strongest acids. Acids falling in the H_0 range from −3 to +3.3 are completely eliminated by steam aging.

Data for hydrofluoric acid treated M-46 catalyst (used) are also shown in Figure 1. This treatment modified the acid-strength distribution curve by reducing the amount of strong acids and increasing the proportion of weaker acids.

Because acid strength distribution curves are relatively smooth and continuous (Figure 1), it suffices (2) for most purposes to consider three ranges of acid strength; weak, pK_a +3.3 to −3.0; intermediate, pK_a −3.0 to −8.3; and strong pK_a −8.3 or less. Referred to the sulfuric acid–water

Table II. Acidity Distribution and Cracking Selectivity[a] of Some Experimental Cracking Catalysts

Catalyst	Code No.	Acidity[b] Meq./G. at H_0		Acidity[b] Meq./Sq. M. × 10^4 at H_0		Gasoline[c] Factor	Coke[d] Factor	Conversion,[e] Vol. %
		+3.3	−3.0	+3.3	−3.0			
Fresh chrome bead	1	0.20	0.19	...	...	0.96	1.30	64.1
Steam-aged M46[f]	2	0.13	0.13	...	...	1.00	1.00	54.7
Steam-aged chrome bead[f]	3	0.12	0.08	6.6	4.3	1.0	1.03	52.6
Steam-aged 4.6% Cr_2O_3-M46[f]	4	0.11	0.09	7.8	6.4	0.98	0.95	54.1
Chrome bead, treated HF vapor	5	0.43	0.05	18	2.1	1.15	0.90	53.5
Same, used	6	0.17	0.07	...	...	1.21	0.86	52.1
Cr_2O_3 on HF-chrome bead	7	0.06	0.04	...	...	1.10	0.70	44.5
Cr_2O_3 on HF-M46	8	0.11	0.03	21	5.7	1.05	0.52	41.5
Chrome bead treated with alcoholic HF	9	0.37	...	14	...	1.17	0.74	56.3
Chrome bead treated HF-H_3PO_4	10	0.23	...	9.5	...	1.13	0.98	62.7
HF chrome bead +0.8% Cr_2O_3	11	0.06	0.04	6.7	4.5	1.10	0.70	44.5

[a] Cracking long range gas oil in a fixed bed reactor at 510° C., LHSV = 1, 20-min. process period, atmospheric pressure. [b] Acidity values refer to acidities stronger than H_0 = +3.3 or −3.0. [c] Ratio of gasoline yield to that for steam-aged M46 at same conversion. [d] Ratio of coke yield to that for steam-aged M46 at same conversion. [e] 100-volume % bottoms. [f] Steam-aged at 732° C. 4 hours in 100% steam.

system, these ranges of acid strength are from 3×10^{-4} to 48% H_2SO_4, 48 to 90% H_2SO_4, and stronger than 90% H_2SO_4, respectively. It is doubtful if acids weaker than 3×10^{-4}% H_2SO_4 have any catalytic significance.

The amount of acidity in these three ranges of acid strength is shown in Figure 2 for a number of commercial cracking catalysts both new and after aging to equilibrium levels in commercial cracking service. This plot permits comparison of the *n*-butylamine titer at each level of H_0 acid strength as well as the amount of acidity in each range of acid strength. Of the clay catalysts, kaolin has the largest proportion of strong acids, while montmorillonite has the least. As a class, clays have a significantly lower proportion of strong acids than synthetic silica-alumina catalysts. Acidity differences between equilibrium clays are considerably less than those observed for corresponding fresh catalysts. The silica-magnesia catalyst has a high level of acidity, nearly two thirds of which is weak acidity. In contrast to the silica-magnesia catalyst described by Benesi (*2*) a significant amount of both very strong and intermediate strength acidity is present.

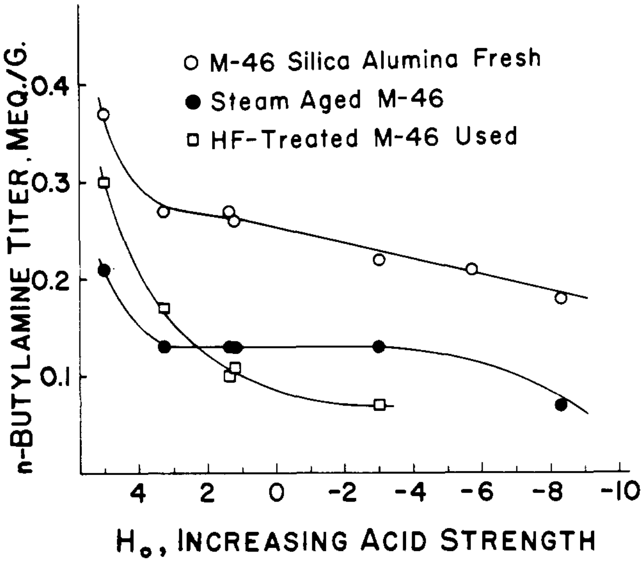

Figure 1. Butylamine titers *vs.* acid strength for three M-46 silica-alumina catalysts

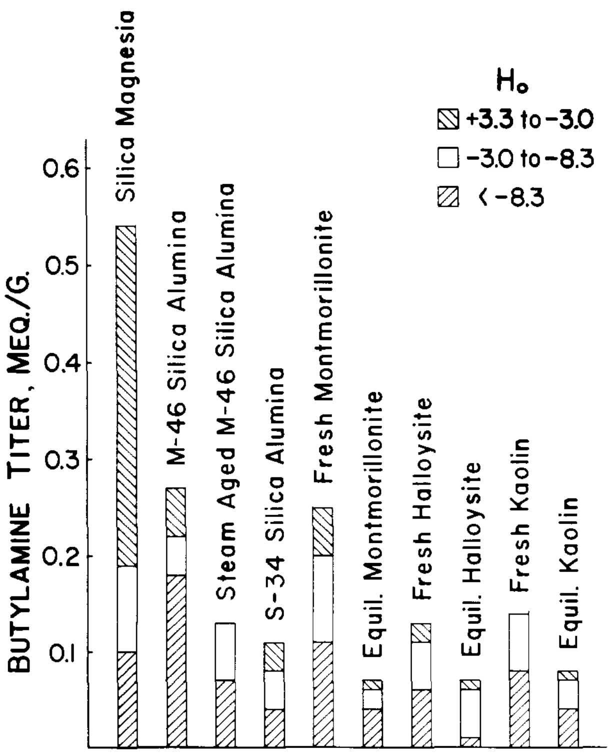

Figure 2. Acid strength distributions of fresh and used commercial cracking catalysts

The gasoline obtained using clay, silica-magnesia, or hydrofluoric acid treated silica-alumina catalysts is lower in octane number than that obtained from silica-alumina catalysts. This fact suggests a relation between the proportion of very strong acids and octane number. Kaolin produces a higher-octane gasoline than the other clays in line with its higher strong acid content.

A relation between relative coking tendency and the amount of acidity stronger than $H_0 = -3$ is indicated by the data summarized in Table II and plotted in Figure 3 for a series of modified silica-alumina catalysts. No correlation is observed when coke factor is plotted *vs.* total acidity at $H_0 = +3.3$; the data are given in Table II. From this we may conclude that acids weaker than $H_0 = -3$ (48% H_2SO_4) contribute very little to coke formation, and that the coke-forming tendency of a catalyst increases with the amount of relatively strong acids present. The conversion was found to be a linear function of the amount of acidity either at $H_0 = +3.3$ or $H_0 = -3.0$.

Figure 4 shows the gasoline selectivity of this same series of catalysts as a function of the acidity per unit area both at 3.3 and −3 H_0 levels. Increasing the concentration of acid

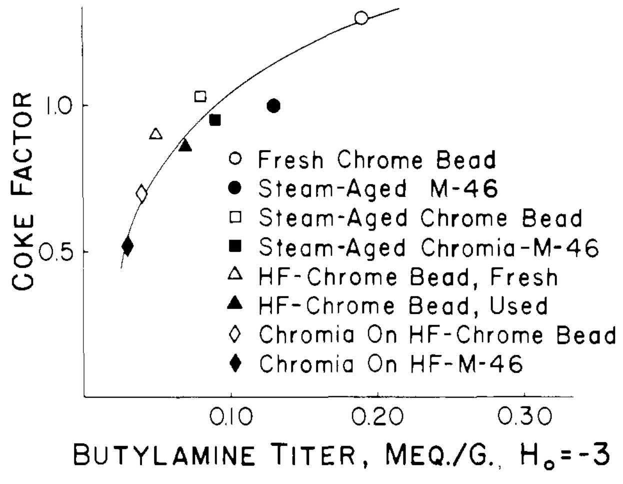

Figure 3. Coke factor *vs.* acidity stronger than $H_0 = -3$ for modified silica-alumina catalysts

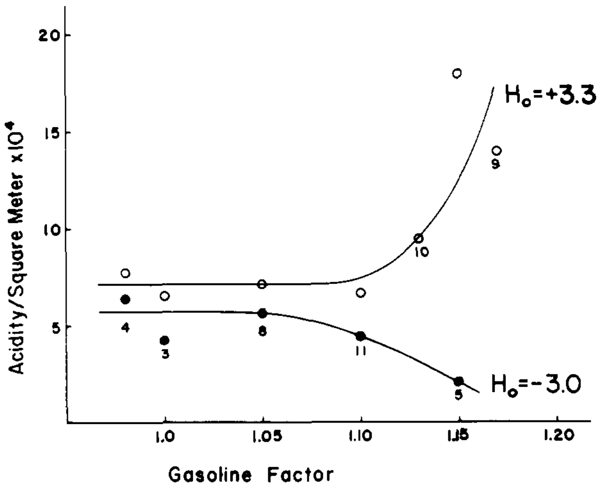

Figure 4. Effect of acid site density on selectively for acidity stronger than $H_0 = +3.3$ and -3.0

sites stronger than $H_0 = -3$ decreases the gasoline selectivity, while the reverse is true at $H_0 = 3.3$. The difference in ordinate between the two curves is the weak acidity per square meter; thus a high concentration of weak acid sites per unit area promotes high gasoline yields.

Acidity Distribution of Platinum-Alumina Reforming Catalysts. Platinum-alumina reforming catalysts activated at 500° C. convert Hammett indicators to the colored conjugate acids in the same manner as cracking catalysts. (The term "reforming" is applied to a process for increasing the octane number of gasoline in which an approximate 121° to 204° C. gasoline fraction is passed over a platinum-alumina catalyst under about 500 p.s.i.g. of hydrogen pressure at 468° to 510° C. The predominant reactions are isomerization of alkylcyclopentanes to alkylcyclohexanes and dehydrogenation of alkylcyclohexanes to alkylbenzenes.) Butylamine titration results for a number of commercial reforming catalysts activated in air are summarized in Table III. Data on several catalysts activated in hydrogen at 450° C. had indicated no effect of reduction on acidity or acid-strength distribution.

The Hammett acidity distribution of the platinum-alumina catalysts differs from that of many cracking catalysts in that practically all the acidity is very strong and no weak acids are present. Many platinum-alumina catalysts have a substantially higher level of acidity than most commercial cracking catalysts.

After use in a commercial gasoline reforming operation for several months, a slight loss in total acidity was observed, as shown by data in Table III. However, the loss of strong acidity amounted to about 40%, with most of this lost strong acidity being converted into acids of intermediate strength. Activation of the powdered catalyst in air at 500° C. before measurement removed the residual coke remaining after regeneration in the plant.

A relation between catalyst acidity and stability under severe (high temperature) reforming conditions is suggested by the data in Figure 5. Operating at a severity level giving an initial F-1 clear octane of 98 to 100, the change in octane level of the reformate after 100 hours on steam is plotted *vs.* acidity in milliequivalents per gram at $H_0 = -3$ for several commercial reforming catalysts. With one exception, the points lie on a smooth curve.

The addition of halogen is not necessary to produce strong acidity in an alumina. [This observation is not necessarily in conflict with the results of Webb (*17*) who reported that hydrofluoric acid treatment increases the acid strength of alumina without altering the number of acid sites.] While F-1 alumina, containing about 0.8% sodium, has no acidity even at $H_0 = +3.3$ when activated at 500° C., removal of sodium by cation-exchange with dilute acetic acid or ammonium salts results in an acid-strength distribution similar to that of chlorided platinum-alumina catalysts. Data for F-1 alumina leached with acetic acid are given in Table III.

The present results are not in agreement with those of Clark, Ballou, and Barth (*3*), who report the absence of strong acids on F-10 alumina and a total acidity of only 0.04 meq. per gram. It is shown in a later section (Table IV) that adsorbed water eliminates strong acidity and reduces the total acidity of F-10 alumina, suggesting the probability that the sample of F-10 used by Clark and others contained adsorbed water.

Acidity Distributions of Some Cobalt-Molybdate-Alumina Catalysts. Data on the acidity distribution and hydrodesulfurization efficiency of several commercial cobalt-molybdate catalysts are summarized in Table V. Over the limited range studied, desulfurization efficiency is a linear function of the acidity stronger than $H_0 = -3$, indicating that hydrodesulfurization requires both an acid function and a hydrogenation function just as in the case of reforming over platinum-alumina catalysts.

Spatial Distribution of Acid Sites. A number of catalysts were titrated with ethylenediamine (EDA) at $H_0 = -3$ hoping that comparison of these data with the butylamine (BA) titer would throw light on the spatial distribution of acid sites. Steric considerations would permit EDA to react

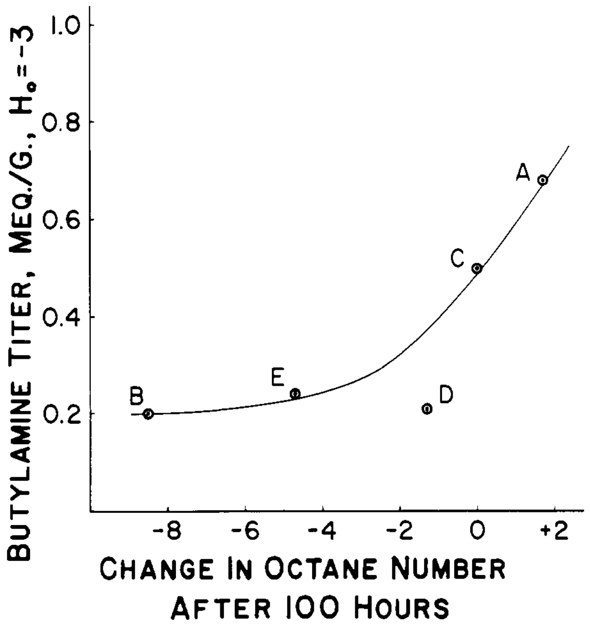

Figure 5. Stability of some commercial platinum-alumina catalysts in reforming straight-run naphtha to initial F-1 clear octane number of 98–100 as a function of catalyst acidity stronger than $H_0 = -3$

Table III. Acid Strength Distribution of Commercial Platinum-Alumina and Alumina Catalysts

		Butylamine Titer, Meq./G. in H_0 Range				
Catalyst	Halogen, %	+3.3 to −3.0	−3.0 to −8.3	<−8.3	Total	Change in Octane No. After 100 Hours[a]
Platinum-alumina A, fresh	0.41	0	0.03	0.65	0.68	+1.7
Platinum-alumina A, used	. . .	0	0.24	0.38	0.62	. . .
Platinum-alumina B, fresh	0.47	0.07	0.03	0.17	0.27	−8.5
Platinum-alumina C, fresh	0.55	0	. . .	. . .	0.50[b]	0
Platinum-alumina D, fresh	0.55	0	0.02	0.19	0.21	−1.3
Platinum-alumina E, fresh	0.57	0	0.03	0.20	0.23	−4.7
Platinum-alumina F, fresh	0.53	0	0.03	0.46	0.49	. . .
F-10 alumina	0.5	0	0.01	0.28	0.29	. . .
F-1 alumina[c]	0	0	0.07	0.19	0.26	. . .

[a] Charge. 129°-196° C. undesulfurized composite (0.023% sulfur). Run conditions. 500 p.s.i.g., 3.0 LHSV, 10:1 recycle ratio, isothermal reactor, temperature adjusted to give 98–100 initial F-1 clear octane number (ASTM Standard D 908-56). [b] *n*-Butylamine titer at $H_0 = -3.0$. [c] Base-exchanged with dilute acetic acid, washed with distilled water, and calcined 5 hours at 500° C.

Table IV. Effect of Adsorbed Water on Catalyst Acidity Distribution

Catalyst	Kaolin		M-46 Silica-Alumina		F-10 Alumina		Platinum-Alumina Reforming Catalyst	
% water pickup of 500° C. dried catalyst from Drierite	0.62		1.0		1.5		2.6	
Moles water adsorbed per acid site	2.5		2.0		2.9		2.2	
Butylamine titer, meq./g. in H_0 range	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet
3.3 to −3	0	0	0.05	0.025	0	0.02	0	0.45
−3 to −8.3	0.06	0.07	0.04	0.08	0.01	0	0.04	0
<−8.3	0.08	0.04	0.18	0.14	0.28	0	0.61	0
Total, <3.3	0.14	0.11	0.27	0.245	0.29	0.02	0.65	0.45

Table V. Acid Strength Distribution of Commercial Cobalt-Molybdena-Alumina Catalysts

Catalyst	Butlyamine Titer, Meq./g. in H_0 Range +3.3 to −3.0	−3.0 to −8.3	<−8.3	Total	% Desulfurization of Middle East Catalytic Gas Oil, 2% Sulfur[a]
A	0	0.06	0.19	0.25	73
B	0	0	0.31	0.31	76
C	0	0.06	0.35	0.41	79

[a] Run condition. 650 p.s.i.g., 385° C., LHSV = 3.

with two acid centers if the spacing were in the range of about 2 to 5 A.

All alumina-base catalysts, including both gamma and eta types, were found to have an EDA/BA molar ratio of 1.0. Certain cracking catalysts, such as halloysite and silica-magnesia, also showed an EDA/BA ratio of 1.0; others, such as fresh M46 and montmorillonite, had anomalously high ratios of 1.7 and 1.9, respectively. For all of this latter group of catalysts, steam aging or use considerably reduced the high EDA/BA ratios (to 1.08 to 1.33).

The apparent inability of EDA to neutralize more than one acid site per molecule indicates either that the acid sites are more than 5 A. apart, or that the second amino group is too weakly basic to effect even partial neutralization of the acid sites. A definite choice between these two possibilities cannot be made at present.

For the silica-magnesia catalyst, the EDA/BA ratio was found to be 1.0 at H_0 = +3.3 as well as at −3.0, even though two thirds of the acid sites are weaker than H_0 = −3. This catalyst also has smaller pores than most of the other catalysts studied. These data appear to eliminate two possible explanations for the high EDA/BA ratios observed with certain cracking catalysts: EDA is too weak a base to react effectively with the weaker acids present on the catalyst or the EDA molecule is smaller and can react with acid sites in small pores not accessible to butylamine.

Modification of Acid Strength Distribution by Adsorbed Water. The effect of water on the acid strength distribution of a series of catalysts was determined by equilibrating the 500° C. dried catalysts for 4 days in a desiccator over Drierite. [The amount of water adsorbed after 4 days may not represent complete equilibrium; nevertheless, the data indicate the relative tendencies of these catalysts to adsorb water at low partial pressures. The principal interest was in the effect of water on acid-strength distribution. Thorough mixing of catalysts before and during acidity titrations (which required several days) enabled the water adsorbed to be redistributed over the catalyst in a manner approximating complete equilibrium.] The vapor pressure of water over Drierite is equivalent to 3.5 p.p.m. of water vapor in the air space of the desiccator. Data on the amount of water adsorbed by each catalyst and its effect on acid strength distribution are given in Table IV. In terms of weight, the two aluminas adsorb substantially more water than the cracking catalysts; in terms of moles of water per acid site, the amounts adsorbed are of the same order of magnitude, ranging from 2 to 2.9 moles per site. However, the effect on acidity is much more drastic for the alumina than for the cracking catalysts. The two aluminas lose all acidity at H_0 = −8.3 compared to 50 and 22% for kaolin and M46, respectively. The intermediate strength acidity (H_0 = −3 to −8.3) actually increases 17 and 100%, respectively, for kaolin and M46, while being eliminated from the alumina. Weak acidity (H_0 = +3.3 to −3.0) appears in both aluminas, although entirely absent from the dried catalyst. In the case of platinum-alumina catalysts, about three fourths of the strong acidity is converted to weak acidity.

The modifying action of water on catalyst acidity is also observed when the effect of activation temperature on the development of acidity is studied. An M-46 silica-alumina catalyst soaked in water and dried at 120° C. actually has a higher total acidity (due to rehydration) than M46 activated at 500° C. as received. On the other hand, an F-1 alumina base-exchanged with dilute acetic acid (to remove sodium) must be heated to nearly 300° C. before developing any acidity even at H_0 = +3.3 and to about 400° C. before developing acidity at H_0 = −8.3.

The Nature of Acid Centers. The nature of the active acid centers on a cracking catalyst has been a point of controversy for some years. While several investigators (*6, 7, 15, 16*) have suggested that protonic acids are the active centers, others (*4, 9, 10, 13, 14*) have argued that Lewis acids are responsible for catalytic activity. The references cited are only a few of those bearing on this question.

The foregoing observations have brought out a number of differences between the acidity of cracking catalysts on the one hand and those of alumina such as reforming catalysts on the other.

Type of acid strength distribution.

Effect of adding back water on acidity and acid strength distribution.

Effect of activation temperature on development of acidity.

Relative ease of neutralization by ethylenediamine and butylamine.

Difference in catalytic cracking activity, although butylamine titration shows many aluminas have much more strong acidity than most cracking catalysts.

In view of the above differences, the acid centers on a cracking catalyst must be of a rather different nature from those present on an activated alumina. If both are Lewis acids, one must postulate a considerable difference in acid strength, with the cracking catalysts possessing the strongest acids (*14*). Results of Hammett acidity measurements do not tend to support this conclusion, although measurements with indicators of lower H_0 than −8.3 are needed. Furthermore, water, as a Lewis base, might be expected to have a greater modifying effect on the strongest Lewis acids; actually, the acidity of cracking catalysts is found to be relatively insensitive to water as compared to the alumina. While a very strong Lewis acid on hydration might become a fairly strong protonic acid (*14*), one would expect a greater change in acid strength distribution than is observed on hydrating an M-46 catalyst. While a detailed discussion is beyond the scope of this paper, acidity measurements suggest that the acid centers on a cracking catalyst may differ in kind, rather than only in degree (of strength), and hence at least a significant and catalytically important fraction of them may be protonic acids, as indicated by the recent work of Holm, Bailey, and Clark (*7*). Other experiments tending to give additional support to this conclusion are in progress and will be discussed in a subsequent paper.

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Preparation and Surface Properties of Porous Titania

E.M. GLADROW and H.G. ELLERT
Esso Research Laboratories, Humble Oil & Refining Co., Baton Rouge, La.

THE PREPARATION OF TITANIA by simple hydrolysis of various titanium salts has been described numerous times in the literature. However, the heat stability of pure hydrous titania, as measured by surface area and pore volume, has not been adequately described. This study was made to define better the heat stability of pure hydrous titanias and of titanias containing known amounts of extraneous metal oxides.

The crystalline form of TiO_2 obtained from the hydrolysis of Ti^{+4} salts is dependent on the particular salt used, the preparative techniques employed, and subsequent heat treatment. Thus, Schossberger (*9*) and Pamfilov and Ivancheva (*7*) show that hydrolysis of $TiCl_4$ in water or dilute ammonium hydroxide yields rutile, whereas $TiO(SO_4)$ gives anatase. Anatase is converted to rutile by calcining at high temperatures (750° to 1800° F.). The transition may be catalyzed (*3, 5*) by dry hydrogen chloride, or aqueous hydrobromic acid; boric acid inhibits the transition. Anatase is transformed to rutile at lower temperatures with chloride present; with sulfate higher temperatures are required. The transition is not sharply defined, but is time-temperature-dependent. Thienchi (*10*) found that on heating anatase at 900° F. for 30 minutes only a trace amount of rutile appeared, whereas after 1 hour the transition to rutile was essentially complete. The transformation of anatase to rutile is irreversible (*8*). Brookite, another crystalline form of TiO_2, has been prepared in admixture with anatase by hydrolysis of ethyl titanate. It is also converted to rutile by heating at 1300° F. or higher (*2, 6*).

EXPERIMENTAL PROCEDURES

Materials. The *n*-butyl, *sec*-butyl, and isopropyl titanates (Titanium Pigment Corp.) were used without further purification. The $TiCl_4$ and $TiO(SO_4)$ were of the best grade commercially available.

Pure Titania. The hydrolyses were carried out in amounts of aqueous media sufficient to obtain form 2 to 10% TiO_2 solids concentration.

Alkyl titanates yielded gelatinous precipitates on hydrolysis in water, dilute ammonium hydroxide, and dilute (ca. 5%) acetic acid. These precipitates were filtered with suction and water-washed. Hydrolysis in 20 to 70% acetic acid gave sols which set to firm, transparent hydrogels when heated to 150° to 180° F.

Hydrolysis of $TiCl_4$ in dilute ammonium hydroxide gave a gelatinous precipitate. Treatment of a cold aqueous solution of $TiCl_4$ with excess ethylene oxide resulted in the formation of a firm hydrogel. On prolonged washing of the