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The Measurement of Catalyst Acidity

I. Titration Measurements

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The *n*-butylamine titration method has been widely used for the measurement of acid strength distributions on solid catalysts. An implicit assumption with this technique is that both the *n*-butylamine titrant and the indicators are in adsorption equilibrium with acid sites on the surfaces. This assumption has been tested and found invalid. Serious doubt is therefore cast on the utility of such methods for the assessment of surface acidity. It is shown that instead of determining an acid site distribution, the total acidity of the sample is usually obtained. Having ascertained the problems involved, an alternative method has been devised for characterizing the site energy distribution. A series of bases of varying pK_a dissolved in one of several solvents was employed. The strong irreversible chemisorption of these yielded distributions quite different from those obtained by the *n*-butylamine technique.

INTRODUCTION

Extensive investigation of acid catalysis during the past 30 years has resulted in major contributions both to fundamental knowledge and to industrial development, particularly in the field of petroleum chemistry. Several reviews dealing with the subject of surface acidity of solid catalysts have recently been published (*1–3*). One of the most widely used methods for measurement of the number of acidic sites of varying strength is known as the Hammett indicator, or the *n*-butylamine titration method. The catalyst surface is generally "titrated" with an amine in nonaqueous solvent and aliquots of catalyst are then tested with a series of Hammett indicators. This method was originally introduced by Benesi (*4*) and has been subsequently modified (*5, 6*).

The use of indicators in acid–base titration is a standard laboratory technique. When dealing with solutions, the assumptions made are quite valid, viz. that chemical equilibrium is maintained at all times, and that the amount of indicator employed is too small to disturb the point of equilibrium appreciably. When one of the reactants is a solid surface, however, both of these assumptions are questionable. Nevertheless, equilibrium has been assumed in titrations of the surfaces of acidic solids. This assumption has been tested in the present work and found to be false.

Besides the above, the titration method has other serious limitations. The most obvious of these is the cumbersome experimental procedure. Moreover, many variables exist which can affect the results. For example Matsuzaki *et al.* (*7*) determined that the number of acid sites obtained by the Benesi method changed from 0.4 to

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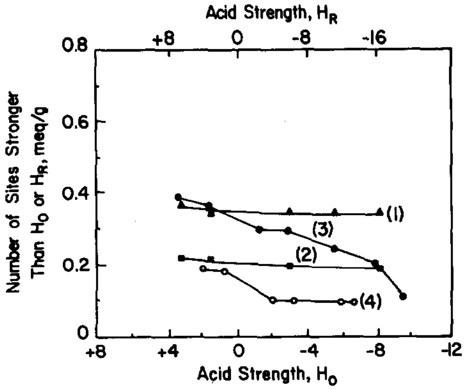

FIG. 1. Acid strength distribution of silica-alumina (6, 10, 5) ▲, ●, and ■ using H_0 indicators, ○ (9) using H_R indicators.

0.6 mmol/g catalyst (on silica-alumina) when the volume of butter yellow indicator (0.1% solution) was increased from 0.05 to 0.2 ml. For the same catalyst the *n*-butylamine titer ranged between 0.3 and 0.5 mmol/g catalyst as the titration time was increased from 6 to 50 hr. These authors (*7*) also found that the *n*-butylamine titer depended upon the catalyst particle size. When the sieve mesh cut was changed from 35–50 to 100–200, the *n*-butylamine titer increased from 0.35 to 0.6 mmol/g catalyst. The *n*-butylamine titer is also affected by the titrant concentration. Balikova (*8*) found that the titration of surface acidity of magnesia-silica with either 10^{-1} or 10^{-3} N *n*-butylamine in benzene using benzeneazodiphenylamine as indicator yielded results differing by 40%. In summary, the *n*-butylamine titer is dependent upon the physical conditions of the experiment. Data for quite similar silica-alumina surfaces from several sources (*5*, *6*, *9*, *10*) are collected in Fig. 1. Hirschler and Schneider (*6*) and Benesi (*5*) found flat acidity distributions; all sites had an acid strength of $H_0 \leq -8.2$ (Curves 1 and 2 of Fig. 1). Delmon *et al.* (*9*) on the other hand, using H_R indicators and Yoneda *et al.* (*10*) using H_0 indicators found weak distributions (Curves 3 and 4 of Fig. 1). Note also that Curve 1 indicates a titer about four times that of Curve 4.

Most of the published results obtained by the Benesi method indicate the presence of only very strong acid sites on silica-alumina and zeolites. These results do not agree with those obtained by other methods. For example, Kevorkian and Steiner (*11*) made microcalorimetric studies of the chemisorption of ammonia and characterized sites of intermediate strength. Kubokawa (*12*) compared his method of determining surface acidity by ammonia desorption with the Hammett indicators method. He wrote, "From the results (obtained with H_0 indicators) it is concluded that almost all of the acid sites on silica-alumina are very strong. On the other hand, the desorption method indicates the presence of weak as well as strong acid sites." Misono *et al.* (*10*) determined the acid strength distribution curve by a gas chromatographic method. They, too, reported a discrepancy between their results and those using Hammett indicators. In a series of papers, Topchieva *et al.* (*13*, *14*) investigated the high-temperature adsorption and desorption of bases on zeolites under chromatographic conditions. In this way the existence of a distribution of acidic centers of varying heats of adsorption was demonstrated. A large drop in energy of activation (33–15 kcal/mol) for desorption was also noted with increasing coverage. Similarly, irreversibly adsorbed ammonia was found and this decreased with increase in temperature. These results provided strong evidence for the existence of a distribution of acidic centers of varying strengths, in contrast with those obtained at room temperature using the indicator methods. The amine titration results indicated only strong sites when indicators of varying H_0 (+3.0 to −8.2) were used with the same preparations.

Recently, Yoneda and co-workers (*15*) made a critical analysis of the conditions required for the establishment of adsorption equilibrium in the *n*-butylamine titration of acid surfaces. They demonstrated that the requirement of adsorption equilibrium of indicator and amine with the acid sites is difficult to satisfy and that the commonly used conditions may lead to substantially higher acidities than the actual values. Balikova (*8*), in studies of the correlations between the activity and acidity of catalysts, found that the establishment of adsorption equilibrium in the titration of acid sites is in some cases a very slow process. In spite of all this, the technique has been useful as evidenced by the fact that it has been made part of many studies in recent years (at least 15 in 1977 alone).

The above-mentioned limitations have been further examined in the present work and a way found to turn them to the advantage of the experimentalist. Irreversible adsorption is the result of a kinetic, not a thermodynamic, limitation. The desorption rate is exponentially limited by the heat of adsorption. Thus on a given surface, bases of increasing strength (pK_a) were found to become "irreversibly adsorbed" in increasing amounts because a critical value of the heat of adsorption could be exceeded on weaker sites with stronger bases. Thus, in this way it should be possible to derive at least a qualitatively correct measure of the acid site distribution. As will be seen, however, such approaches can never be made quantitative because of solvent effects and other limitations. Moreover, a "correct" method will be described in a subsequent paper. Consequently, the experimental details herein have been abbreviated.

EXPERIMENTAL

Equipment

The liquid circulation system is shown diagrammatically in Fig. 2. It consisted of a Research Appliance Company stainless-steel liquid micro-bellows pump (A) which connected the pot (B) filled with liquid to the top of the catalyst column (C). The pumping rate was adjusted at the pump so as to maintain a level of liquid above the catalyst of about 4 cm. The glass column was about 30 cm long and 1 cm in diameter while the length of the catalyst bed inside the column was about 8 to 10 cm. The column could be surrounded by a 20-cm-long split furnace, which was used with flowing O_2 as required for pretreatment. The system was filled with dry purified He during the experiments and the system was sealed with Teflon stopcocks. A septum (D) was mounted on the pot so that liquids could be injected or samples removed for analytical purposes.

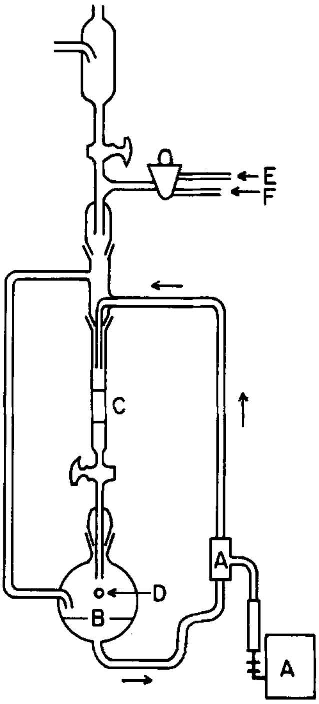

FIG. 2. Liquid circulation system, (A) liquid microbellows pump, (B) pot, (C) catalyst column, (D) septum, (E) oxygen flow, (F) nitrogen flow.

A three-way stopcock was connected to the top of the column to admit flowing oxygen or helium. Liquid samples from the pot were analyzed on a Microteck G.C. 2000R gas chromatograph. The 6 ft × $\frac{1}{4}$-in.-o.d. column was packed with 7% NaOH and 40% carbowax 20M on Chromosorb W, 60 to 80 mesh. It was operated at 100°C and with a helium flow of about 50 cm^3/

TABLE 1

Properties of Catalysts Studied[a]

Catalyst	Surface area (m^2/g)
γ-Al_2O_3	192
Molybdena/γ-Al_2O_3 (oxidized)	185
Molybdena/γ-Al_2O_3 (reduced)	185
Silica-alumina (M-46)	250

[a] It was assumed that the area of catalyst M-46 did not change on base-exchange with Na^+, Ba^{2+} or Ca^{2+}.

min. These conditions gave the best separation of the different bases and solvents used.

Purification of Carrying Gas and Reagents

The oxygen was purified by passage over a mixture of anhydrous $CaCl_2$ and $Mg(ClO_4)_2$. Nitrogen, hydrogen, and helium gases were purified by passing first over these same drying agents and then through an activated charcoal trap at the temperature of liquid nitrogen.

Several different solvents and organic bases were used. Benzene from the Aldrich Chemical Company (thiophene free) was further purified by passing over activated silica-alumina and then distilled and stored over sodium. Just before use, the benzene was again passed over activated silica-alumina, to ensure removal of any poisons which could affect the experiments.

Other solvents such as isooctane, ether, and pentane were purified by passing over activated alumina before distilling. Before use, they were passed over activated silica-alumina.

The Hammett indicators phenylazonaphthylamine ($pK_a = +3.3$), benzeneazodiphenylamine ($pK_a = +1.5$), and dicinnamalacetone ($pK_a = -3.0$) were purchased from Eastman Kodak Company. Benzalacetophenone ($pK_a = -5.6$) and anthraquinone ($pK_a = -8.2$) were obtained from Aldrich Chemical Company. Solutions of these indicators (10^{-2} *M*) were used without further purification.

Solutions (1 *M*) of the adsorbate bases (Aldrich) in various solvents were used in the titration procedure. The *n*-butylamine was dried with KOH and distilled from BaO; pyridine was refluxed over KOH(s) followed by fractional distillation; 3-picoline was dried over CaO and fractionally distilled; diethylether was passed over activated alumina three times, distilled, and again passed over alumina just before use; acetone was dried with anhydrous $CaSO_4$ and then distilled; 2,6-dimethylpyridine was distilled from $AlCl_3$ (14 g/100 ml).

Catalysts and Catalyst Pretreatments

One of the catalysts was the much studied Houdry M-46 silica-alumina. Derivatives of it were made by base exchange with Na^+, Ba^{2+}, and Ca^{2+}. These catalysts were prepared by contacting the M-46 with solutions of the acetate salts of the desired cations. This was followed by washing with distilled water. The resulting catalysts contained 0.684 mequiv Ba^{2+}/g catalyst, 0.25 mequiv Ca^{2+}/g catalyst, and 0.25 mequiv Na^+/g catalyst, respectively. Other catalysts used were γ-alumina (Ketjen CK300), and 8% molybdena/γ-alumina (oxidized and reduced). The latter had been prepared from the alumina by the incipient wetness method (*16*). It was reduced in flowing H_2 (*16*) for about 4 to 5 hr at 525°C. Table 1 shows the surface areas of these catalysts.

Procedures

The catalysts (Fig. 2) were pretreated in dry oxygen overnight at about 520°C; the catalyst was then washed with helium at the same temperature for about 1.5 hr before cooling in flowing dry helium to room temperature. Then 100 ml of dry solvent was added to the pot via the septum as the He flow was continued. The liquid was circulated at such a rate that the catalyst was continuously covered with solvent. Base used to titrate the surface was injected into the liquid in the pot by a syringe. The solution circulated onto the top of the catalyst, through the column of catalyst, and back into the pot which served as a reservoir. A fresh sample of catalyst was used for each experiment.

The molybdena/alumina was first oxidized by flowing dry oxygen overnight at 520°C; then it was washed with dry helium for 1.5 hr, before dry hydrogen was passed for 5 hr at the same temperature; this treatment was followed by dry helium flow for 1.5 hr before cooling in He to room temperature.

In tests of the ability of the system to achieve equilibrium several different types of experiments were made, but always the amounts of reagents used per unit weight of catalyst were similar to those required for the *n*-butylamine titration technique. In one type, 100 cm^3 of 10^{-4} *M* indicator solution, or about 1.2×10^{18} molecules/g of catalyst (5 g of dry catalyst were used) were injected into the pot and the resulting solution was circulated over the catalyst for about 24 hr or more. Up to 10 times as much indicator was tested with only qualitative changes in the results. In a second approach, known amounts (see Fig. 4) of 1 *M* *n*-butylamine solution were injected into the pot and the solution was circulated slowly (100 cm^3/hr) for about 18 hr. After 24 hr of circulation, small increments of indicator solution were added (6×10^{17} molecules/g of catalyst) and circulated. This type of experiment was repeated starting each time with a new and freshly pretreated aliquot of catalyst, but different amounts of *n*-butylamine were used before testing with (different) indicators. Data for each of these experiments were recorded as color photographs.

An adsorption isotherm was determined in a third type of experiment. The pretreated catalyst was first contacted with 100 ml of circulating dry solvent and then measured aliquots of 1 *M* base solution were added successively to the pot. These usually were 1 ml of 1 *M* solution, i.e., they contained about 1.2×10^{20} molecules of base per gram of catalyst. After each such addition, circulation was continued and 7-μl samples were removed periodically from the pot and analyzed by glc until either no detectable base remained or else its concentration reached a constant time invariant level. The glc analyses, together with solution volumes, provided data from which the amount of base left in the solution could be determined. Given the initial amount, and the amount left in the pot, the amount adsorbed could be calculated as a function of the equilibrium concentration in the pot. Repeated additions of base were made in the manner described above until the entire surface became saturated. In this way, the adsorption isotherm was defined for each particular base.

In a second step of the same experiment, the column was isolated from the system, and flushed with several liters of dry solvent to desorb the weakly held base. This solvent was not circulated and was checked periodically by glc until no more base could be detected coming from the catalyst. The amount of solvent required to desorb the reversibly adsorbed base was determined using a large sample (50 μl) of the solution coming out of the column. This amount of solvent was found to fall in the range 2.0 to 2.5 liters. While the catalyst was being flushed, the rest of the circulating system was washed very carefully with the solvent, to make sure that no base was left on the walls. At all times precautions were taken to protect the catalyst from atmospheric moisture by keeping it immersed in dry solvent.

Finally, the column was again connected to the system and recirculation of solvent was initiated. The adsorption isotherm was then redetermined and the difference between the two isotherms was defined as chemisorbed base. This method of adosrp-

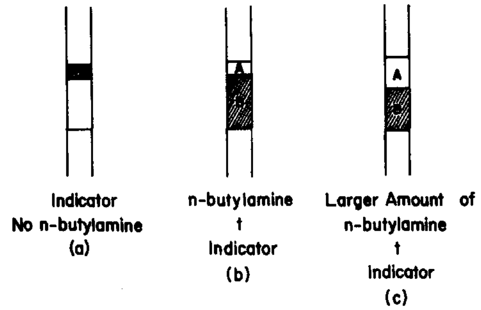

FIG. 3. Demonstration of the nonequilibrium system on M-46 where (A) is the portion of column covered with *n*-butylamine and (B) is the portion covered with indicator. Indicators tested are listed below:

Indicator	Basic color	Acid color	pK_a
Phenylazonaphthylamine	yellow	red	+3.3
Benzeneazodiphenylamine	yellow	red	+1.5
Dicinnamalacetone	yellow	red	−3.0
Anthraquinone	colorless	yellow	−8.2

tion–desorption–readsorption was applied to the following different systems:

(a) *n*-Butylamine as base and benzene as solvent with catalysts M-46, M-46 + Na^+, M-46 + Ba^{2+}, and M-46 + Ca^{2+}.

(b) Different bases (*n*-butylamine, 3-picoline, pyridine, ether, or acetone) in benzene solution on M-46 and M-46 + Ba^{2+}.

(c) Pyridine (as base) and isooctane (as solvent) on alumina and on 8% molybdena/alumina (oxidized and reduced).

(d) Other solvents (ether, benzene, isooctane, pentane) were used with pyridine on M-46 to establish the importance of competition with solvent. In addition, experiments made in the absence of solvent (except N_2); these will be described in a later paper.

(e) The chemisorptions of pyridine and 2,6-dimethylpyridine in isooctane were compared on catalysts M-46 and on alumina to test for effects of steric hinderance of the basic nitrogen atom.

In one experiment, after saturating the alumina surface with 2,6-dimethylpyridine, pyridine was added in small aliquots and the amounts of both bases were determined from the solution in the pot.

RESULTS

Studies with Hammett Indicators

These basic molecules were quantitatively removed from the circulating liquid at the top of the catalyst column, where they were adsorbed as their conjugate acids. For small amounts of indicators (comparable with the "end points" of the titration technique), only the top part of the catalyst column (about 1 cm) became colored in the acidic form. The remainder of the column remained white even though benzene was circulated for long periods of time (24–48 hr). There was no evidence of spreading of the indicator band. This was true for all indicators and catalysts tested.

Adsorption of n-Butylamine and Testing with Indicators

In a similar manner, *n*-butylamine adsorbed in a band at the top of the column. Thus, when an indicator was added to the pot and circulated, the molecules bypassed this band and adsorbed just below it, as indicated in Fig. 3. The upper part of the catalyst maintained its original white color, but the indicators adsorbed below this region exhibited the color of their acidic forms. Evidently *n*-butylamine neutralized the acidic sites in the upper part of the column and thus no sites were available for the adsorption of the indicator. Circulation for long periods of time before adding the indicator did not spread or move the *n*-butylamine molecules down the column, nor were they eluted by the indicator.

When different amounts of *n*-butylamine were added, the length of the uncolored region varied accordingly. The column length covered with *n*-butylamine was measured in each case after adding small aliquots (10^{18} molecules/g) of one of the indicators. These data, plotted as the amount of *n*-butylamine adsorbed vs uncolored column length, are shown in Fig. 4. They show that each increment of length is essentially fully covered before coverage of the next increment begins. Moreover, the data measure the capacity of the catalyst to hold *n*-butylamine irreversibly in benzene wash at room temperature (extrapolation of curves to abscissa = 1.0).

Studies of n-Butylamine Adsorption

The rate of *n*-butylamine uptake by the silica-alumina surface M-46 is shown in Fig. 5. The solutions contained initially about 0.2 and 1.0 mequiv/g of the amine for the two experiments shown. When 0.2 mequiv/g of catalyst (Curve A) was circulated, no *n*-butyalmine was left in the solution phase, i.e., all *n*-butylamine was retained by the catalyst. Conversely, when 1.0 mequiv/g catalyst was used (Curve B), only a portion of the total amount was retained on the catalyst surface (0.73 mequiv/g catalyst). The remaining concentration in the liquid phase did not vary further with circulation time up to 24 hr.

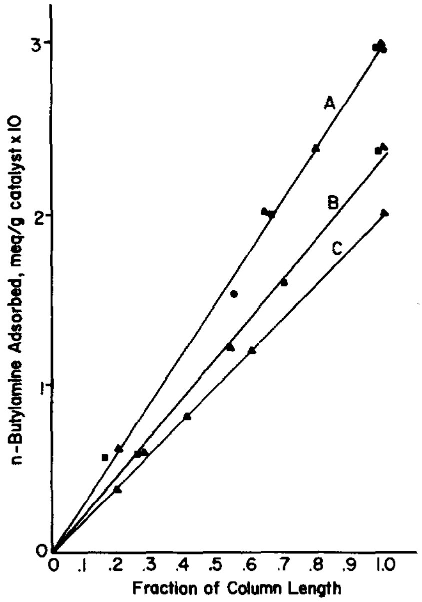

FIG. 4. Relation between *n*-butylamine adsorbed and fraction of column covered with *n*-butylamine. A = M − 46; B = M − 46 + Ba^{2+}; C = M − 46 + Na^+. Different points are for different indicators: ▲, $pK_a = +1.5$; ■, $pK_a = -3.3$; ●, $pK_a = -5.6$.

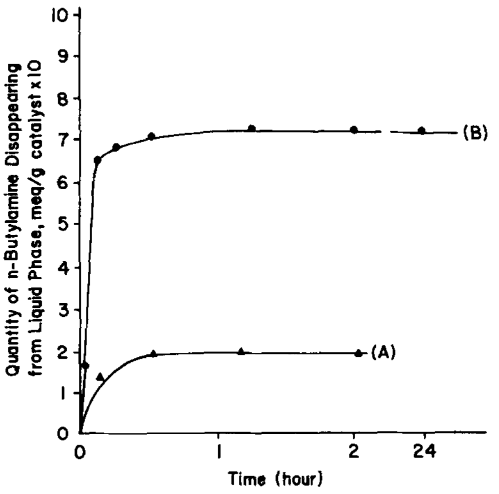

FIG. 5. *n*-Butylamine uptake by M-46 as a function of time.

A catalyst series, composed of M-46, M-46 + Na^+, M-46 + Ba^{2+}, and M-46 + Ca^{2+}, was examined using *n*-butylamine as adsorbate. Two isotherms were derived as described in the experimental section: the total adsorption (reversible plus chemisorption), and the reversible adsorption. A circulation period of 2 hr was used between base additions. Figure 6 shows one such set of data and the results for all

TABLE 2

Adsorbed *n*-Butylamine on M-46 and Doped M-46; Titer, mequiv/g Catalyst

	M-46	M-46 + Ba^{2+}	M-46 + Ca^{2+}	M-46 + Na^+
$H_R{}^{a,b}$	0.35	0.28	0.28	0.19
$H_0{}^{b,c}$	0.22	0.19	0.18	0.16
Circulation method	0.30	0.24	0.27	0.19
Breakthrough method[d]	0.30	0.24	—	0.20

[a] 44′4″-Trimethoxytriphenyl methanol, pK_a = 0.82.

[b] Ref. (*21*).

[c] Butter yellow, pK_a = 1.5.

[d] Benzeneazodiphenylamine, pK_a = 1.5.

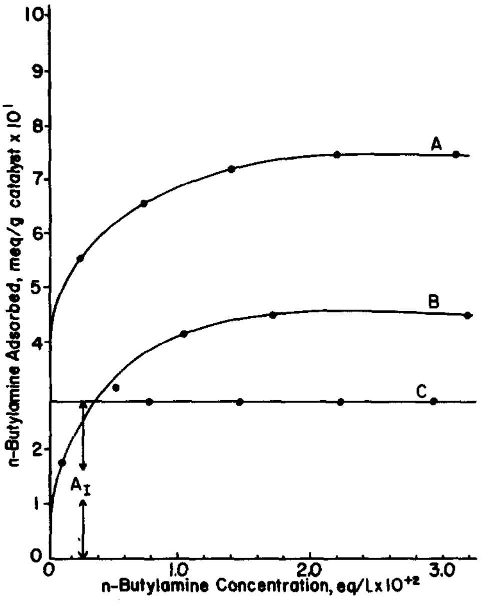

FIG. 6. *n*-Butylamine adsorption on M-46 against its concentration (adsorption isotherm). (A) Total *n*-butylamine adsorbed, (A_I) irreversibly adsorbed *n*-butylamine, (B) reversibly adsorbed *n*-butylamine, and (C) irreversibly adsorbed *n*-butylamine.

catalysts studied are compared with results of titration experiments in Table 2. It is apparent that the amine chemisorption measures the same sites as the H_R indicator method, i.e., total acidity.

Curve A of Fig. 6 is a measure of the total adsorption of *n*-butylamine on the fresh catalyst. The second adsorption isotherm was determined (Curve B) after flushing with about 2 liters of benzene. (The majority of the reversible portion of the base was removed by the first 500 ml.) The difference between Curves A and B measured the irreversible chemisorption (Curve C). The zero intercepts of C were in good agreement with the amount of *n*-butylamine adsorbed before a detectable amount remained in solution (A_I). They were also in agreement with the breakthrough intercepts of Fig. 4.

TABLE 3

Adsorption of Bases on M-46 and Doped M-46

Base	pK_a	Titer (mequiv/g catalyst)	
		M-46	M-46 + Ba^{2+}
n-Butylamine	10	0.30	0.24
3-Picoline	5.7	0.14	—
Pyridine	5	0.12	0.09
Ether	−3	0.06	0.04
Acetone	−5	0.08	0.06

Acid Site Distribution

The adsorption, desorption, and readsorption method described above was applied using bases of different strengths to characterize the distribution of acid sites on silica-alumina (M-46 and M-46 + Ba^{2+}). The bases used ranged in strength from pK_a = +10.0 (strong) to pK_a = −5 (weak). The irreversible adsorption of the base was taken as a count of acid sites corresponding to a specific pK_a. Table 3 presents the results including the bases used and their corresponding pK_a's. A distribution of acid sites can be derived from these data (the weakest base measuring the

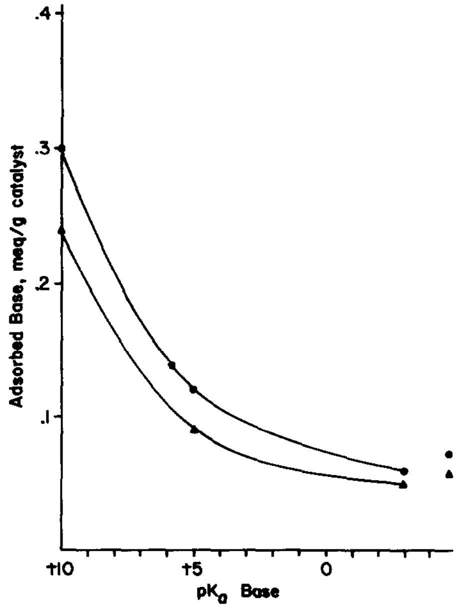

FIG. 7. Distribution of acid sites as a function of the pK_a of the bases used for the determination. Data are for ● M-46 and ▲ M-46 + Ba^{2+}.

number of strongest sites). Figure 7 shows the amounts of irreversibly held base (mequiv/g catalyst) or number of sites having an acidity greater than the corresponding pK_a. The amount of irreversibly held base ranged from 0.30 to 0.06 mequiv/g catalyst for M-46 and from 0.24 to 0.04 mequiv/g catalyst for M-46 + Ba^{2+}. For each base used, more was adsorbed on M-46 than on M-46 + Ba^{2+}. The acetone points may be a little high because of a small amount of polymerization. These data may be contrasted with those of Fig. 1.

Solvent Effects

In the experiments described above, benzene was the only solvent used. The effect of changing solvents on the amount of irreversibly adsorbed pyridine was investigated by the same techniques. Solvents of varying base strength were used. These solvents ranged from ether, which is a relatively weak base, to N_2, which is considered to be neutral. Table 4 shows the different solvents used along with the corresponding amounts of irreversibly adsorbed pyridine. It is obvious that competition with the solvent makes an important contribution to the result obtained. This seriously clouds the quantitative interpretation of such data.

Application to a Colored Surface (Reduced Molybdena/Al_2O_3)

The same procedures can be applied to colored (or black) surfaces. The adsorption of pyridine from isooctane solution was determined for γ-Al_2O_3 as well as for oxidized and reduced 8% molybdena/γ-Al_2O_3 (*16*). The reduced catalysts were black after reduction with $H_2(g)$ at 500°C. Table 5 shows the results, including the total amount of pyridine adsorbed as well as the irreversibly adsorbed pyridine. The γ-Al_2O_3 surface had a higher capacity for pyridine adsorption than either the oxidized or the reduced forms of molybdena/Al_2O_3. The method does not discriminate between Brönsted and Lewis acids!

TABLE 4

Effect of Solvent on Pyridine Titer, mequiv/g Catalyst

Solvent	Ether	Benzene	Isooctane	Pentane	N_2[a]
Pyridine adsorbed	0.04	0.12	0.18	0.35	0.85

[a] From microbalance data to be reported later.

TABLE 5

Adsorbed Pyridine (mequiv/g Catalyst)

Catalyst	Total amount of pyridine	Irreversibly adsorbed pyridine
Al_2O_3	0.77	0.55
8% molybdena/Al_2O_3 (oxidized)	0.61	0.38
8% molybdena/Al_2O_3[a] (reduced, black)	0.68	0.42

[a] Estimated extent of reduction is e/Mo, 1.5 e/Mo.

Hindered Amine

The same methods were applied to compare the chemisorption of pyridine and 2,6-dimethylpyridine on silica-alumina and on alumina. The results of this work

TABLE 6

Irreversible Adsorption of Pyridine and of 2,6-Dimethylpyridine from Isooctane Solution on Silica-Alumina (M-46) and Alumina (at Room Temperature)

Catalyst	Amine adsorbed (mequiv/g catalyst)	
	2,6-Dimethylpyridine	Pyridine
Silica-alumina	0.350 [0.031][a]	0.18 [0.036][a]
Alumina	0.15 [0.013][a]	0.50 [0.06][a]

[a] Values in brackets are results from Benesi (*17*). Data obtained from chromatographic desorption method at 400°C.

are shown in Table 6 where they are compared with data reported by Benesi (*17*) for similar surfaces. More pyridine was adsorbed on γ-Al_2O_3 than on silica-alumina; conversely, more 2,6-dimethylpyridine was adsorbed on silica-alumina than on Al_2O_3.

DISCUSSION

Critique of Benesi Method

According to the Benesi hypothesis, at adsorption equilibrium *n*-butylamine should be uniformly distributed over the entire surface with the strongest acid sites populated first, etc. Thus, the adsorption of any of the indicators onto the surface after it has reached adsorption equilibrium with the *n*-butylamine should cause the surface to become uniformly colored. Equilibrium could not be achieved with the present system; *n*-butylamine adsorbed very strongly at the top part of the column and the desorption–adsorption cycle did not occur at an appreciable rate (Fig. 3). The indicator, which was introduced later, adsorbed on the next available sites which were just below the *n*-butylamine band. When larger aliquots of *n*-butylamine were used, a linear relationship was found between the portion of column length covered and the amount of *n*-butylamine added (Fig. 4). The data show clearly that each increment of length is essentially completely covered with *n*-butylamine before coverage of the next increment begins. Obviously, such experimental conditions cannot be used to deduce energy site distributions, as suggested previously. The result of the so-called "titration" appears to be a measure of the total acidity stronger than a critical value instead of a site distribution and the numerical result will depend on the solvent employed. Moreover, as observed (*4–6*), nearly the same *n*-butylamine titer should be expected, irrespective of which Hammett indicator is used.

Other techniques have reflected the distribution of acid sites of varying strength on similar surfaces. These include experiments involving heats of adsorption and those where energies of activation for desorption have been measured. The equilibrium problem can be avoided if the surface is first saturated and then desorption commenced. Now the weakest sites will empty first. Consequently the amount of irreversibly adsorbed base remaining as a function of desorption temperature may be used as a measure of the distribution, as in these cases the desorption is limited by the activation energy for desorption, i.e., by the heat of adsorption.

Recognition of the fact that equilibrium cannot be attained under the conditions of the titration experiments provides some insight into the variability that has appeared in the literature. The effect of such variables as indicator or base concentration, solvent effects, and length of "equilibration time" on the titration results (*7*, *8*) can be related to the nonequilibrium nature of the adsorption process.

In spite of the discrepencies in the literature, the argument has been advanced (*6*) that if these data are not correct they are at least useful. Repeated attempts have been made to correlate the titration method with the activity of acid-catalyzed reactions. One of the possible reasons for the occasional success or failure of such attempts can now be seen. Since the *n*-butylamine titration method does not measure a distribution of acid strengths and may, in fact, measure the total acidity, the correlation, or lack of it, should depend on the system being investigated. Those systems which depend upon the total acidity should correlate, while those which depend on only a portion of it may not. Thus, Andreu *et al.* (18) investigated the cracking of alkylbenzenes over a series of silica-alumina preparations containing 5, 10, 18, 25, and 50% Al_2O_3 and attempted to correlate these rates with the *n*-butylamine acidity. Maximum acidity was obtained at an alumina content of approximately

25% while only minor differences in the conversions of *t*-butylbenzene (at 280°C) and *sec*-butylbenzene (at 380°C) were observed over the entire series. The lack of agreement between acidity and activity measurements may arise because the titration method measured total acidity, while the activity depends on the number of Brönsted sites of a certain strength. The total acidity can be obtained more simply and directly by amine adsorption determinations such as those described herein which eliminate many factors which can affect the titration measurements.

Development of Alternative Methods

The total amount of irreversibly adsorbed base was estimated from the difference between two adsorption isotherms of Fig. 6. The total (maximum) adsorption of *n*-butylamine on M-46 was 1.8×10^{14} molecules/cm^2. Interestingly, the total amount of adsorbed pyridine was very similar to the number of hydroxyls remaining on the surface of M-46 following pretreatment (*19*), i.e., about 1 to 2×10^{14} OH/cm^2.

The irreversible portion was identical with the difference (C) between the two isotherms (total minus reversible). Moreover, this portion was in good agreement with results of the titration method. Thus, the amounts of irreversibly adsorbed *n*-butylamine and the titration end points as well were found to be a measure of the total number of acid sites. *n*-Butylamine is a strong base and, as such, would be expected to adsorb on sites of all strengths. This irreversibly adsorbed amount was shown to be the same as that required to prevent the adsorption of any of the indicators in their acidic form completely (Fig. 4). The amounts of irreversibly adsorbed *n*-butylamine on M-46, M-46 + Ba^{2+}, and M-46 + Na^+ from the isotherms were 0.31, 0.24, and 0.18 mequiv/g catalyst, respectively, compared with 0.30, 0.24, and 0.20 mequiv/g catalyst required to prevent the indicators from adsorbing in their acidic form.

Since chemisorption measures total acidity stronger than a critical value, by using adsorbed bases with a range of pK_a values, a meaningful distribution could be developed (Fig. 7). This distribution differs substantially from those derived from the titration method. With the former, a distribution of sites of varying strength is indicated; with the latter a flat distribution was found (*4–6*).

The heat of adsorption, and hence the activation energy for desorption, of a base will depend upon both its pK_a and the intrinsic strength of the acid. Strong bases like *n*-butylamine ($pK_a = +10$) will chemisorb on all sites of interest. Reagents having moderate basicities (such as pyridine or picoline of $pK_a = +5.0$ and $+5.7$), should adsorb on moderate and strong acid sites, while weak bases such as ether or acetone (of $pK_a = -3$ and -5) will interact with only the strongest acid sites. Hence, the irreversible chemisorption of this series of bases on a solid surface should provide a measure of the true acidity distribution. This can be rationalized by assuming that for any base on the same surface,

$$\text{rate of desorption} = M\nu e^{-E_d/RT}$$

in which M is the amount adsorbed, ν is the frequency factor, and E_d is the activation energy for base desorption. As the reversibly adsorbed base is desorbed and M approaches A_I (the amount of irreversibly held base), the rate of desorption approaches zero. At the limit, E_d will take on some critical value which should be the the same for any base. Thus A_I measures the number of sites having $E_d >$ the critical value. As weaker and weaker bases are employed, adsorption sites must become more and more acidic to attain the critical value.

As expected the chemisorption of *n*-butylamine was larger than that of any other base on all catalysts studied. By definition, it measured total acidity of these surfaces. The differences between the values for *n*-butylamine and pyridine for M-46 and M-46 + Ba^{2+} are a measure of the number of weaker acid sites. Ether adsorbed only on the strongest sites. The count of these sites, on these catalysts, was 0.06 and 0.04 mequiv/g catalyst, respectively. The number of sites of moderate strength estimated from the values for pyridine and ether were 0.06 and 0.05 mequiv/g catalyst, respectively, for the two catalysts. Thus, introduction of base exchange ions affected all sites, weak and strong, a conclusion also reached by Hirschler using his titration method (*6*).

The acidity distributions determined as plots of irreversibly adsorbed base as a function of pK_a (Fig. 7) resemble those obtained by certain physical techniques, particularly the temperature-dependent irreversible chemisorption of nitrogen bases such as pyridine. The shapes of the curves are similar; an initially large decrease in the ordinate occurs with an increasing temperature (from 100 to 200°C) just as in the present experiments with decreasing pK_a of the base (from +10 to +5). We can thus identify that amount of irreversibly adsorbed pyridine which is removed between 100 and 200°C with that located on the weak acid sites, i.e., those requiring strong bases (pK_a between +10 and +5). In a like manner, pyridine desorbed above 200°C represents the stronger sites which are capable of holding the weaker bases (pK_a less than +5).

Our method utilized a nonequilibrium property of the system for determining an acid site distribution for solid surfaces. In contrast to the *n*-butylamine titration method, a distribution of acid sites was observed. Advantageously, it may be applied to colored or black surfaces since it does not require the use of an indicator.

Effect of Different Solvents

When pyridine was adsorbed from solution in ether, benzene, isooctane, pentane, or carried by $N_2(g)$ (Table 4), the adsorption increased in the following order: ether < benzene < isooctane < pentane $< N_2(g)$; this is also the order in which basicity of the solvent decreases. Consequently it is the order in which the competition between pyridine and solvent for adsorption sites decreases. Competition for adsorption between the solvent and base may be explained on the basis of simple Langmuir theory of competitive adsorption (*20*). For a dilute solution of strongly adsorbed base A in solvent B

$$\theta_A = 1 - \frac{K_B C_B}{K_A C_A}$$

$$\theta_B = \frac{K_B C_B}{K_A C_A}$$

in which the θ's represent fractional surface coverages of the solid, the K's the thermodynamic equilibrium constants, and the C's the concentrations. It is assumed here that $C_A < C_B$, $K_A > K_B$, and $C_A K_A > C_B K_B$. Even though K_B may be much smaller than K_A, θ_B will not become negligible, even at relatively high values of C_A, because of the huge excess of solvent. Thus, the fraction of the sites covered by pyridine, at equilibrium, when adsorbed from different solvents, will depend upon the strength of interaction between the solvent and the surface as well as on the pyridine concentration. When K_B approaches zero, as in the case of N_2, maximum coverage will be achieved. On the other hand, with solvents like ether ($pK_a = +3.0$), the competitive chemisorption will be much more pronounced as observed (Table 4).

The amount of pyridine adsorbed irreversibly from benzene solution on the Houdry M-46, which prevented the indicator benzeneazodiphenylamine ($pK_a = +1.5$) from adsorbing in its acidic form, was 0.12 mequiv/g catalyst. Therefore, with larger amounts of pyridine being adsorbed from isooctane, pentane, or nitrogen solution, the indicator would not be expected to adsorb in its acidic form. In fact, none of the Hammett indicators turned to their acidic form after pyridine was adsorbed from nitrogen at room temperature. Accordingly when different solvents are used in the titration experiments (*5*), varying *n*-butylamine titers will be found, emphasizing once again the qualitative nature of the previously presumed quantitative experiments. From the foregoing discussion it can be seen that for a more quantitative assay solvent effects must be eliminated or at least minimized and that adsorption techniques at elevated temperature will be required. Our results with a flow microbalance have confirmed this and will be reported shortly.

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