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Heats of Adsorption of Ammonia on Silica-Alumina Catalysts and Their Surface Energy Distributions*

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Adsorption isotherms and calorimetric heats of adsorption of ammonia at 0°C were determined on a series of commercial silica-alumina cracking catalysts, namely, virgin, heat-deactivated, steam-deactivated, and used catalyst. The fraction of acid sites and the magnitudes of the site energies vary with the history of the catalysts. The initial heat of adsorption is about 9–15 kcal/mole and decreases to a minimum at about $\theta = 0.1$, then increases sharply. The adsorbate–adsorbate interaction is strikingly high. A procedure of Adamson and Ling was used to find site-energy distributions of the catalysts. There are two predominant site energies, one at about 7 and another at 13.7 kcal/mole. The relationship between acid sites and relative "D + L" cracking activity is discussed.

INTRODUCTION

Silica-alumina cracking catalysts have been shown to have surfaces characterized by centers of high acid strength (*1–4*). Because the surface acidity of catalysts plays an important part in petroleum processing and because of the interest in other applications, considerable research has been done on the measurement of the acidity, and the relationship between acidity and catalytic activity. The methods that have been used to measure surface acidity are: titration in aqueous solution with KOH, evolution of CO_2 from Na_2CO_3 solution, hydrolysis of sucrose, evolution of CH_4 with Zerewitinoff reagent, quinoline adsorption, uptake of ammonia, and titration with amine in nonaqueous systems (*3, 5*).

While these methods would give a quantitative result for the total amount of acid centers, they would not, in general, differentiate between acid strengths. Silica-alumina catalysts have acidic active sites that differ in the strength of the acidity. An attempt to find a distribution of acid site strengths has been made by Benesi (*5*), by titration with amine in nonaqueous medium using various dye indicators. The present contribution describes another technique by which the fraction of acid sites and site-energy distributions may be obtained, *as well as* qualitative or quantitative differences between catalysts that have been treated in various ways. A basic gas, ammonia, was selected as an adsorbate for studying these solid surfaces.

The measurements of adsorption isotherms and calorimetric heats of adsorption of ammonia were undertaken on virgin, heat-deactivated, steam-deactivated, and used catalysts. The ammonia adsorption by such highly heterogeneous surfaces could be a complex phenomenon since chemisorption, physical adsorption, and capillary condensation may occur simultaneously. Nevertheless, the energy of chemisorption of ammonia provides a measure of acid

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strength, and the method is probably more quantitative than any others that have yet been devised for such heterogeneous solid surfaces.

TABLE 1
SILICA-ALUMINA CRACKING CATALYSTS

Designation	Composition and treatment	Surface area (m^2/g)	Relative "D + L" cracking activity
T-B	25% Alumina on silica, fresh	525	42.3
T-B-1	25% Alumina on silica, heat-deactivated from T-B	250	36.3
T-B-2	25% Alumina on silica, steam-deactivated from T-B	248	28.7
T-B-3	25% Alumina on silica, plant equilibrium of T-B	61	15.0

EXPERIMENTAL

The commercial silica-alumina catalysts, listed in Table 1, were kindly supplied by courtesy of Dr. M. C. Throckmorton of the Texaco Research Center, Beacon, New York.

The heat and steam deactivation, and activity determination were carried out at the Texaco Research Center. The heat deactivation was made at about 805°C for 17 hr in the presence of dry air in a muffle furnace, while steam deactivation was done at 565°C under 100 psig steam pressure for 1 hr.

The specific surface areas of the catalysts obtained from nitrogen adsorption at 77.5°K based on the BET method, taking the cross-sectional area of the nitrogen molecule as 15.4 Å^2, are included in Table 1.

Ammonia with stated purity of 99.9% was obtained from the Matheson Company. The gas was admitted to an evacuated system, liquefied at −78°C, dried over metallic sodium, and then subjected to two bulb-to-bulb distillations. Only the middle fraction of the distillate was collected and stored in a 2-liter storage bulb.

The calorimeter used for measuring differential heat of adsorption of ammonia on the catalysts is shown in Fig. 1. This is a modified form of the calorimeter developed by Beebe *et al.* (*6*). It consists of a removable platinum cylinder, B, 5.2 cm long, 1.1 cm in diameter, 0.4 mm in thickness, which serves as sample container, into which are closely fitted seven small platinum tubes serving as fins (cross section is shown in Fig. 1). The central tube is the housing for heater.

A thermal junction of copper-constantan (B and S No. 30) thermocouple wires is silver soldered near the bottom part of the

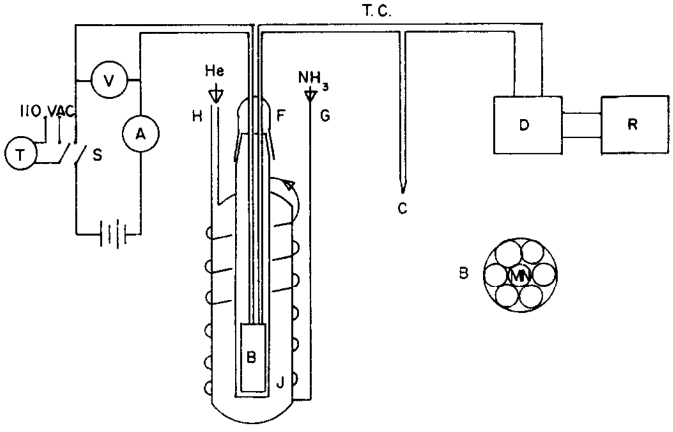

FIG. 1. Calorimeter. A, Milliammeter. B, Platinum bucket. C, Cold junction. D, DC Amplified. F, Cap with male-female joint. G, Adsorbate inlet tube. H, Helium inlet tube. J, Outer jacket. R, Recorder. S, Switch. T, Timer. V, Voltmeter.

platinum cylinder to measure the heat release. Surrounding the Pyrex glass tube which holds the platinum cylinder is a glass jacket, J. The cold junction of the thermocouple is immersed in a glass tube containing pump oil to prevent direct contact with ice in the ice-water mixture. The same Dewar vessel was used for both cold junction and temperature control.

Gas inlet, G, consists of a 3-mm capillary tube coil of six turns which serves as a cooling coil for inlet gas. The heat exchange capacity of the cooling coil was tested by introducing helium into the calorimeter and no temperature change on the thermal junction of the thermocouple was confirmed. The 15-mm tube, H, is connected through stopcocks to the vacuum manifold as well as to a helium reservoir.

The electrical heating element of 150 ohms resistance was made from 5-mil glass-insulated nichrome wire by winding it one layer thick on a 2-mm glass rod.

To measure differential heats of adsorption, about one gram of powder sample, as received, was weighed into the platinum bucket and loaded in the calorimeter which was then inserted into a high vacuum system. The whole calorimeter was outgassed for at least 40 hr at 250–260°C until a residual pressure of 10^{-5} torr was obtained. The calorimeter then was cooled and immersed in the constant temperature base at 0°C under a pressure of 10^{-6} torr for overnight to attain temperature equilibrium.

A measured amount of adsorbate was introduced into the calorimeter and the emf developed on the thermocouple from the heat of adsorption was amplified and sent to a recorder. The catalyst slowly lost the adsorption heat to its surroundings and gradually re-established the thermal equilibrium. Then, a calibration was made by sending a known amount of electrical energy through the heater in the calorimeter, generating another heating–cooling curve on the recorder. When the temperature returned to equilibrium, the equilibrium pressure was read to determine the amount of ammonia which adsorbed and caused this heat release. The heat evolved in the adsorption was determined by comparing the area under the recorded time–temperature curve with that of the calibration curve.

This process was repeated numerous times, adsorbing more small doses until an appreciable part of the surface was covered. A separate calibration was made for every measurement because of different heat capacity in the successive measurements arising from different equilibrium gas pressures and different amounts of adsorbate on the adsorbent.

During measurements the outer jacket of the calorimeter was filled with helium at about 10 torr, permitting the temperature of the calorimeter, after its initial rise, to fall back more rapidly to its equilibrium temperature. The process, therefore, is *isothermal.*

In addition to the adsorption isotherms obtained from the heat measurements, adsorption isotherms were also determined separately by means of two different volumetric systems, one for the range 0.01–200 μ and the other for the range 100 μ–20 cm Hg. The high pressure system was also used for measuring BET surface areas of the catalysts. Outgassing of the adsorbents was conducted at 260°C and 1×10^{-5} torr for a minimum of 40 hr. New samples of the catalyst were used in every run to eliminate any possible "poisoning" from previous runs.

The current for calibration was supplied by twelve 1.5 volt dry cells (3 in series, 4 rows in parallel). This capacity provided a steady current for calibration. The length of the heating period was measured by a standard electric timer which could be read to ±0.01 sec. The current and voltage were read by a DC voltmeter (Weston Model I) and a DC ammeter (Weston Model I). The scale of both meters could be read to ±0.01, volt and milliampere, respectively. The emf from the thermocouple was amplified by a Beckman DC breaker amplifier (Model 14) and recorded by a Leeds and Northrup voltage pen recorder (Speedomax type G, Recorder Model S). The whole apparatus was shielded from any possible stray emf's.

The relative catalytic activity is expressed as "D + L" units (per cent distillate to 400°F plus distillation loss),

$$\frac{\text{volume of liquid product—volume of gas oil.}}{\text{volume of liquid product}}$$

The data are based on unit weight as received. The determination was made by passing refined gas oil at a charge rate of 920 cc/hr through 400 g catalyst at 500°C for a half hour.

RESULTS AND DISCUSSION

Heats of Adsorption of Ammonia on Catalysts

The results of the measurements are shown in Figs. 2–5, for the fresh, heat-deactivated, steam-deactivated, and plant equilibrium catalysts. The data were not corrected for the deviation from ideal gas law and the heat of compression of the gas

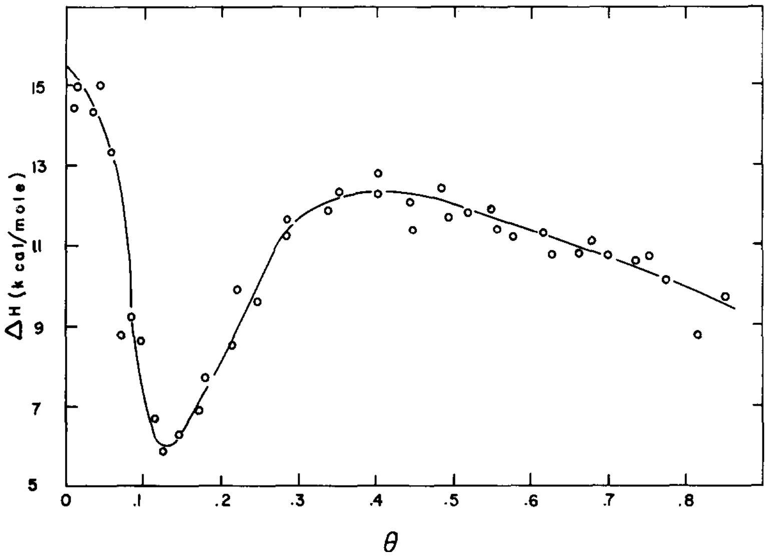

FIG. 2. Differential heat of adsorption of ammonia on fresh catalyst, T-B, at 0°C.

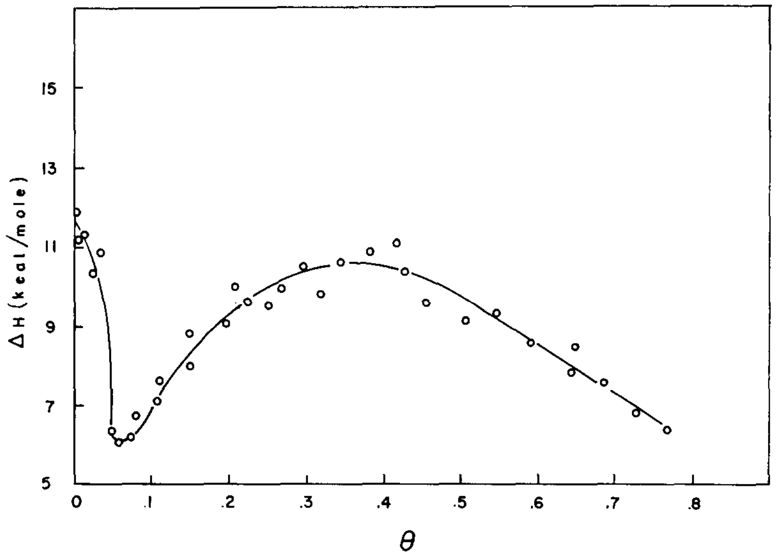

FIG. 3. Differential heat of adsorption of ammonia on heat-deactivated catalyst, T-B-1, at 0°C.

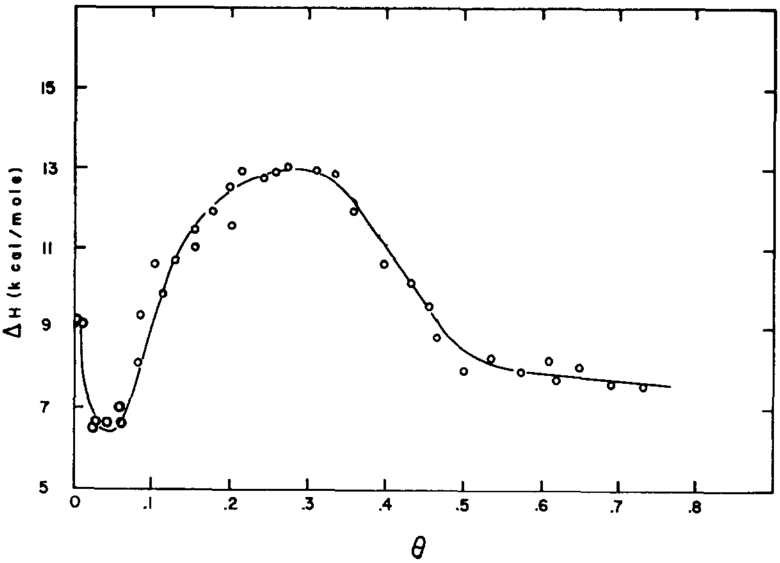

FIG. 4. Differential heat of adsorption of ammonia on steam-deactivated catalyst, T-B-2, at 0°C.

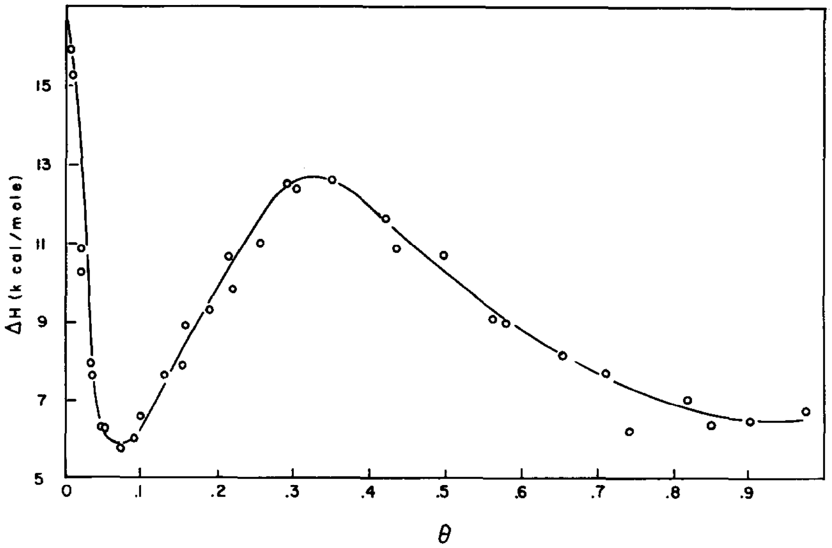

FIG. 5. Differential heat of adsorption of ammonia on used catalyst (plant equilibrium), T-B-3, at 0°C.

within the calorimeter. These corrections would not substantially reduce the over-all error of ±4%.

Estimations of the monolayer capacity for ammonia, V_m, which was needed for computing the fraction of surface coverage, θ, were based on the specific surface areas obtained from nitrogen BET determinations, taking the cross-sectional area of the ammonia molecules as 16 Å^2 at 0°C.

The initial heat of adsorption is high and decreases to a minimum at about one-tenth of the surface coverage, then increases sharply to a peak at about $\theta = 0.4$ and finally decreases gradually. Differential heats of adsorption were all higher than the heat of evaporation of ammonia at 273°K, which is 5.15 kcal/mole. The first high-heat fraction of the heat curve is considered to be due to a combination of effects: (a) protons combining with NH_3 to form NH_4^+; (b) hydroxyl groups forming hydrogen bonds with NH_3; (c) Lewis acid sites combining with NH_3. The following facts are pertinent:

1. Infrared studies of adsorbed ammonia on cracking catalysts by Mapes and Eischens (*7*) indicated that a small fraction of NH_4^+ existed, although a quantitative amount was not given.

2. Recently, the protonic acid content of silica-alumina catalysts of various compositions after different heat treatments was determined by Holm, Bailey, and Clark (*8*), by base exchange with 0.1 *N* ammonium acetate solution followed by pH measurement. The maximum acid content was reported as 18 meq $\times$ $10^{-4}/m^2$. When minimum points of the heat curves are considered to be the points at which the reaction of protons with ammonia is completed, proton acid contents of 17.9, 10, 6.2, and 12.5 meq $\times$ $10^{-4}/m^2$ are calculated, respectively, for T-B, T-B-1, T-B-2, and T-B-3 catalysts. Materials of different sources make it impossible for direct comparison of the results of Holm, Bailey, and Clark and those of the present work; nevertheless the results are of the same order of magnitude.

3. Infrared studies of physically adsorbed polar molecules and the surface of a silica adsorbent containing hydroxyl groups by Folman and Yates (*9*) led them to conclude that: "The adsorption bond due to the surface OH group is very strong even after 6 hr evacuation at 450°. This indicates that these OH groups are chemically bound to the surface; under such conditions of evacuation all water molecules would have been removed." It is, however, generally believed that when the catalyst is heated to 800°C most of the hydroxyl groups on the surface are driven off. This point will be discussed further.

4. Hydrogen bonding effects, ascribed to hydrogen bonding between physically adsorbed molecules and the hydroxyl groups present on the surface of porous silica glass, have been reported by Folman and Yates (*10*), using length-change and infrared techniques. They found that ammonia gives an exceptionally strong hydrogen bond with the surface.

The results cited above indicate the existence of each of three types of surface interaction with ammonia. The present results unfortunately are unable to distinguish which portions of the heat effect belong to each.

Heats of adsorption of ammonia on highly graphitized carbon blacks, according to Beebe's measurement (*11*), were about 6.3 kcal/mole over the whole surface except for a higher heat (about 7.5 kcal/mole) at low surface coverage. The initial higher heat was held to be due to hydrogen bonding between the ammonia and a small fraction of an oxygen complex present on the carbon surface. According to Titoff (*12*), first molecules of ammonia on charcoal showed a differential heat of adsorption of 11.27 kcal/mole; the values passed through a minimum of 7.83 kcal/mole and then increased to 8.71 kcal/mole as more ammonia was adsorbed. This increase was said to be due to mutual van der Waals' forces between adsorbed molecules. Compared with those results, the present increases of differential heats of adsorption after passing through the minimum at about $\theta = 0.1$, are too large to be considered merely as induced dipole and/or mutual van der Waals' interactions between the adsorbed molecules. The following explanation seems preferable.

As discussed previously, the initial part of the adsorption of a basic anhydride such as ammonia corresponds to a neutralization of the surface acid of all types and may be thought of as "salt formation" of NH_4^+, as well as producing highly polarized NH_3 molecules. When all surface acid has been neutralized, the differential heats of adsorption reach a minimum value; on further adsorption, ammonia molecules interact with the NH_4^+ ions and polarized NH_3, to which they are bound by coulombic forces; they also interact by nonpolar van der Waals' forces with the catalyst surface. The coulombic interaction, the force of which is described by an inverse square law, provides for a much higher heat of interaction than can reasonably be postulated by the inverse sixth power law that describes van der Waals' interaction. The experimental heat curves show an initial value of $d\Delta H/d\theta$ of about 35 kcal/mole, which is about 10 times the value calculated for van der Waals' interaction by the equation $d\Delta H/d\theta = 2\ a_2/b^2$ (*13*). The differential heats continue to increase until about four NH_3 molecules are "coordinated" with each NH_4^+ on the surface. The large interaction heats that are observed make the postulate of a surface coordination complex reasonable.

After about one-half of the surface has been covered the additional forces emanating from chemisorbed molecules gradually decrease with further coverage and finally the heat of adsorption reaches the order of magnitude of that found in the case of ammonia on carbon blacks, near the completion of a monolayer.

Fresh catalyst, T-B, has the highest heat for first adsorption and heat-activated, T-B-1, has an intermediate value, while the steam-deactivated one, T-B-2, has the lowest initial heat. This last material, however, has the greatest rise after passing the minimum. The used catalyst has an initial heat as large as that of virgin catalyst, and the rise after the minimum value is about the same as that of steam-deactivated, while the last part after the maximum heat is similar to the heat-deactivated catalyst. It is generally believed that used catalysts suffer both steam and heat deactivation effects. The initial heat of adsorption for the used catalyst was surprisingly high. But this appears to confirm the findings by Kiselev and co-workers (*14*) that the acidity of used catalyst is the same as that of fresh catalyst.

From the heat curves, it may be concluded that about 10% of the surface is heterogeneous with respect to ammonia adsorption, whereas the remainder, or greater part, can be considered homogeneous. This can also be seen from the site-energy distributions found from the isotherms, which will be discussed later. Quinoline chemisorption also showed that the sites per unit of surface area is small (*15*). Since about one-tenth of the surface is heterogeneous a more detailed quantitative description of the strength and distribution of the acid sites may be obtained by redesigning the pressure measuring apparatus for low surface concentrations.

Adsorption Isotherms

The adsorption isotherms for ammonia on these catalysts cover wide pressure ranges. Appreciable amounts of the adsorp-

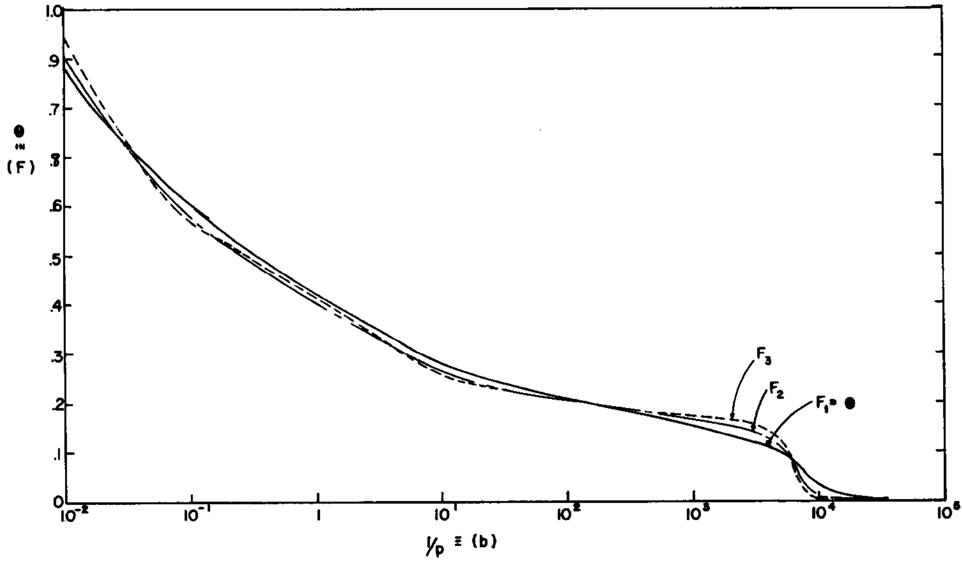

FIG. 6. Adsortpion of ammonia on fresh catalyst,T-B, at 0°C. F_2 and F_3 are succesive F vs. b plots.

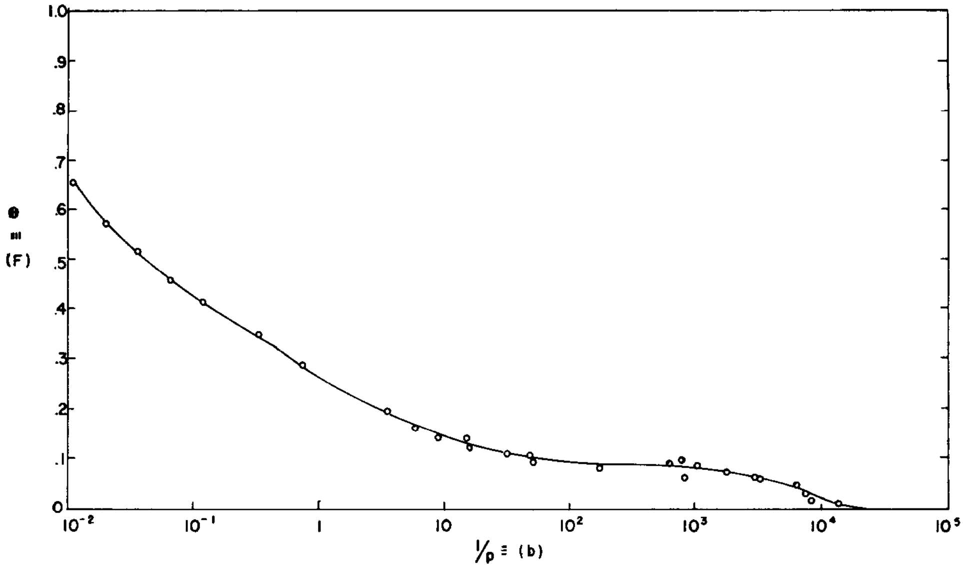

FIG. 7. Adsorption of ammonia on heat-deactivated catalyst, T-B-1, at 0°C.

tion took place at the very low pressure region. Two typical isotherms for the fresh and heat deactivated catalysts are presented in Figs. 6 and 7, respectively.

The Site-Energy Distributions

An attempt was made to obtain the energy distributions from the adsorption isotherms. Of the several attempts to obtain the site-energy distributions (*16*, *17*), particularly those of very heterogeneous surfaces, that of Adamson and Ling (*18*) appears most satisfactory in that fewer *a priori* assumptions are necessary.

For an adsorbent surface having noninteracting regions, each of constant adsorption energy, the experimental isotherm **H** may be expressed as:

$$\mathbf{H} = \left[\int_0^\infty f(Q)\theta(P, T, Q)\, dQ\right]_{P,T}$$

where: $f(Q) = dF/dQ$ is a site-energy distribution function, F the fraction of sites with energy $\geqslant Q$, the adsorbate–adsorbent interaction energy, and $\theta\ (P,T,Q)$ the isotherm function representing adsorption for regions obeying local isotherm θ. It is necessary to assume that the active sites consist of patches, the local isotherms of which obey the Langmuir isotherm,

$$\theta = bP/(1 + bP)$$
$$b = b_0 e^{Q/RT}$$

Strictly, Langmuir's adsorption isotherm cannot be applied to a broad range including fixed and mobile adsorption. However, the present method for determining site-energy distributions appears to be rather insensitive to the isotherm selected. This equation was used in the recent work of Clark and Holm (*19*). Present data also show good fit in the region of mobile adsorption, which may be fortuitous. The collection of constants, b_0, for ammonia includes an area per molecule, σ°, and a characteristic adsorption time, τ°; values of 16 Å^2 and 10^{-13} sec were used, respectively; b_0 was 7.9×10^{-8} at 0°C and pressure in units of mm Hg. The value of b_0 which includes an entropy term is not necessarily constant with surface coverage; the variation of b_0 may not be so sensitive as to give entirely different distribution curve.

Details of the calculation procedure are given by Adamson and Ling (*18*).

Site-energy distributions obtained are shown in Fig. 8 for four catalysts of different history. There are two predominant site energies, one at approximately 7 and

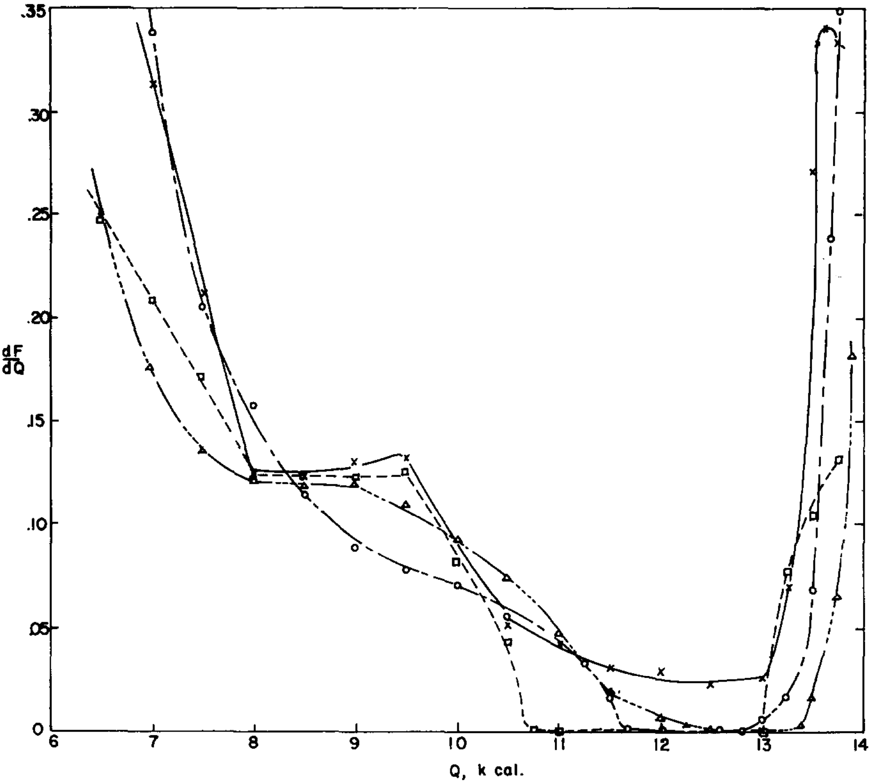

FIG. 8. Differential site-energy distributions for fresh catalyst (×), heat-deactivated (□), steam-deactivated (△), and used catalyst (○).

another at approximately 13.7 kcal/mole. Even with the assumption made in this method the agreement with the calorimetric heat data is strikingly good. It is also noted that the sites having energies of 11–13 kcal/mole are relatively few or nonexistent. Heat and steam deactivations reduced the higher energy sites. The steam-deactivated catalyst has a narrower band at a high energy peak than the heat-deactivated catalyst. This narrow band of high energy sites was missed during the calorimetric measurements; it would have been detected if smaller doses had been used. The heat deactivation undoubtedly reduced the high energy sites of 11 kcal/mole and up. This also can be seen in Figs. 9 and 10. The site-energy distributions of the virgin catalyst, T-B, outgassed at two different temperatures, i.e., 260°C (40 hr) and 800°C (11 hr) are compared with the heat-deactivated catalyst, T-B-1, in Fig. 9. The one outgassed at the higher temperature is more similar to the heat-deactivated catalyst. Further examination of the heating effect at high temperature was made on the steam-deactivated catalyst. This time outgassing was carried out at 500°C for 15 hr, and compared with the same material outgassed at 260°C and with the heat-deactivated catalyst as shown in Fig. 10. It can be seen that the high energy sites decrease from heating and by outgassing at high temperature; the catalyst then becomes more like the heat-deactivated catalyst.

As mentioned previously, most of the hydroxyl groups on the surface would be driven off when the catalyst is heated at high temperature (800°). Complete elimination of the high energy fraction was not obtained even at 800°C. This is supporting evidence that initial high heats are partly due to hydroxyl group on the surface.

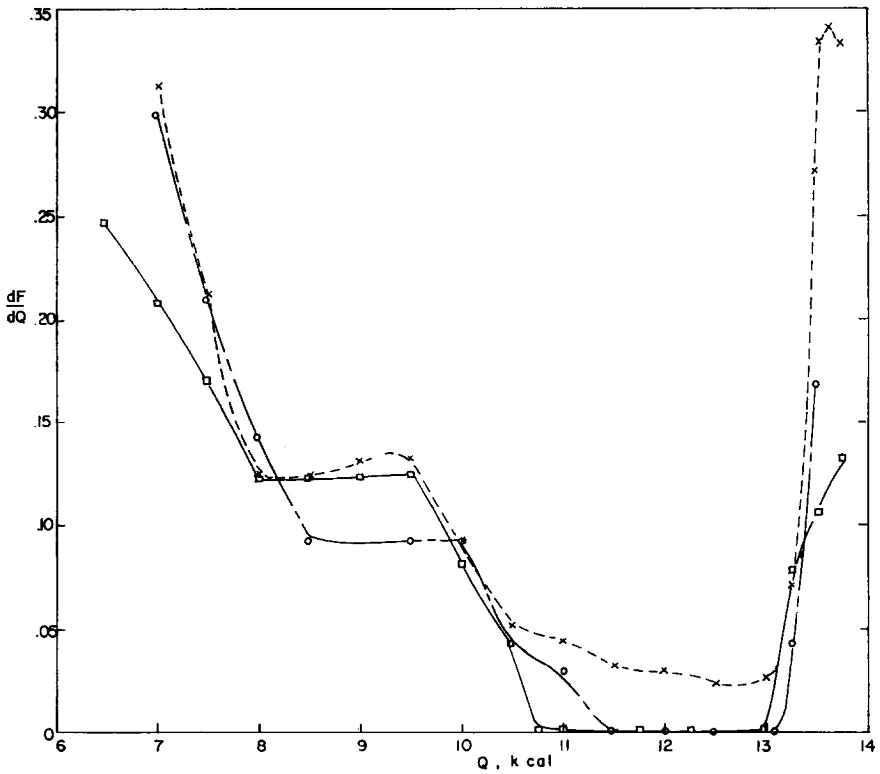

FIG. 9. Differential site-energy distributions for fresh catalyst outgassed at 260° (×), outgassed at 800° (○), and heat-deactivated catalyst (□).

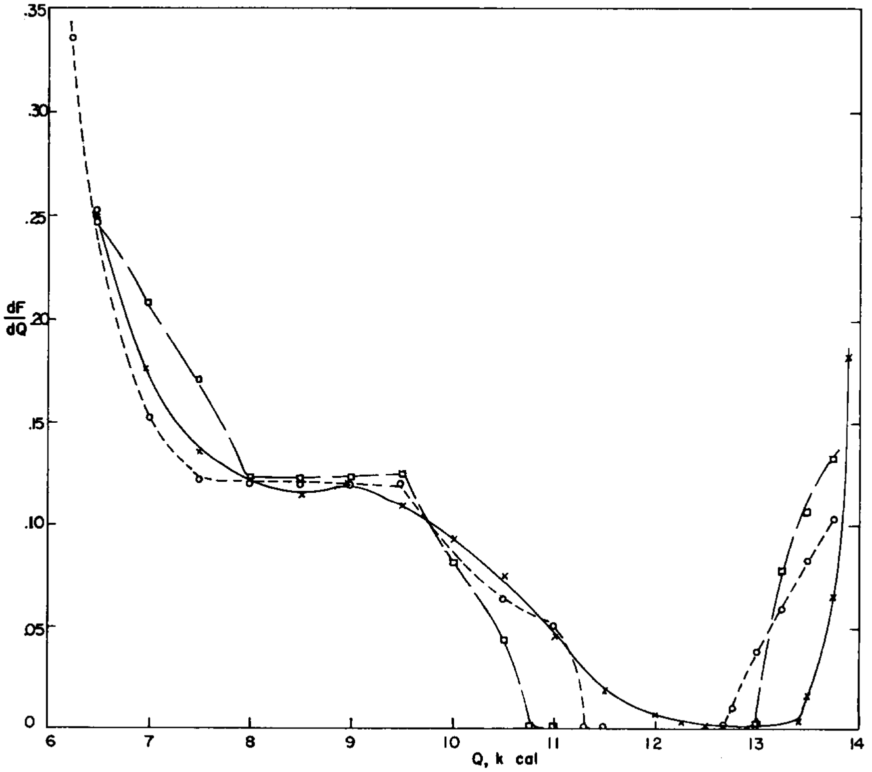

FIG. 10. Differential site-energy distributions for steam-deactivated catalyst outgassed at 260° (×), outgassed at 500° (○), and heat-deactivated catalyst (□).

Outgassing at high temperature reduced the surface area of the catalysts. The specific area of fresh catalyst was reduced to 302 m^2/g from 525 m^2/g by heating at 800°, while that of the steam-deactivated was reduced to 220 m^2/g from 248 m^2/g by heating at 500°C in vacuum.

Cracking Activity and Acid Sites

The series of events thus postulated for ammonia adsorption is clearly determined by the presence of acid sites on the surface of the catalysts. The results do not necessarily mean that only proton acidity is essential to the activity of these catalysts. An attempt to correlate energetic sites with relative "D + L" cracking activity faces a few difficulties. Higher relative activity does not necessarily mean a better catalyst. The practical evaluation of catalysts must include both yield and quality of the cracking products. There is a question whether ammonia adsorption can be considered to serve as a model of the behavior of hydrocarbons under conditions of catalytic cracking on these surfaces. The site-energy distribution depends on adsorbate–adsorbent combinations, as well as on temperature. Temperatures of 450–500°C are generally used for catalytic cracking. The fresh catalysts do not remain fresh for long and the strongest sites may be quickly put out of action catalytically during the determination of the activity. Their high surface areas are very susceptible to sintering or reduction by other mechanisms, and the activity values obtained might not then refer to the same adsorbents that were used for ammonia adsorption.

It is believed that the surface area cannot be considered to be of exclusive importance to catalytic activity. When catalytic activity is reckoned on the basis of each square meter of surface available, the catalysts range themselves in order T-B-3, T-B-1, T-B-2, and the fresh catalyst T-B. This last solid has high surface area to nitrogen molecules of 525 m^2/g, which is a definite indication of the presence of pores of close to molecular dimensions. It is not unreasonable to conclude that much less surface than this is available to hydrocarbon molecules, and that, in any event, so large a surface area is soon reduced to less than half its original value during the cracking reaction of the activity measurement.

It is not possible from the results of this work to clearly define the effect of the most energetic of the acid sites on catalytic activity. A more thorough analysis of the products of the catalytic reaction is required, to discover in what manner qualitative differences of acidity on the catalyst surface affect the quality of the yield.

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