[CONTRIBUTION NO. 98 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

# The Acid Strength of Surfaces

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The acid or basic properties of solid surfaces are interesting aspects of surface structure, and important in the fields of ion exchange and heterogeneous catalysis. Peculiarly, however, systematic study has been restricted largely to *stoichiometry*, the measurement of the combining capacity of surfaces. The purpose of this paper is to approach the problem from a rather different angle and to consider the possibility of defining and measuring relative surface acid *strengths*. While the experimental results of this paper are only semi-quantitative they serve to establish the principles of the approach, so it seems desirable to present them at this time.

**Definition of Acid Strength.**—The most useful basis for the comparison of acid strengths of different media appears to be upon their ability to donate a proton to a neutral base, *i. e.*, in terms of the $H_0$ function of Hammett and Deyrup[1,2] defined as

$$H_0 \equiv -\log a_{\mathrm{H}^+} f_{\mathrm{B}}/f_{\mathrm{BH}^+} \qquad (1)$$

where $a_{\mathrm{H}^+}$ is the activity of hydrogen ion and the $f$'s, the activity coefficients for a neutral (*i. e.*, uncharged) base, and its conjugate acid. The value of the $H_0$ function arises, first, from the fact that, as predicted by theory for media of high dielectric constant, the ratio $f_{\mathrm{B}}/f_{\mathrm{BH}^+}$ is essentially independent of the particular base employed, and, second, because the addition of a proton to an uncharged reactant molecule is, or precedes, the rate-determining step in a great number of acid-catalyzed reactions, thus providing a basis for comparing rates of acid-catalyzed reactions in different media.[2,3] Further, as pointed out by Lewis and Bigeleisen[4] the measurement of the ability of a solvent to convert a base to its conjugate acid may be extended as well to media containing "Lewis acids" (*i. e.*, electron acceptors) rather than proton donors (although here the $H_0$ function will have a rather different meaning). In fact, these authors have interpreted indicator color changes in strong and fuming sulfuric acid as involving, at least in part, the formation of indicator–$SO_3$ complexes. The scope and success of the $H_0$ function treatment of acidity in homogeneous media suggests a similar definition for the acidity of a solid surface: *the ability of the surface to convert an adsorbed neutral base to its conjugate acid.* In the case that the conversion involves the usual proton transfer, this permits the assignment of an $H_0$ function to the surface identical with that defined in equation (1) with activities and activity coefficients those for components in the adsorbed layer. If, on the other hand, the base forms a complex with the surface by virtue of the latter having the properties of a Lewis acid, the $H_0$ function will have a different meaning

$$H_0 = -\log a_{\mathrm{A}} f_{\mathrm{B}}/f_{\mathrm{AB}}$$

where $a_{\mathrm{A}}$ is now the activity of the Lewis acid or electron acceptor. The utility of such a definition of acid strength will depend, as in the homogeneous case, upon the constancy of the ratio of activities, *i. e.*, upon the existence of a single scale of acidities, as defined above, for all surfaces regardless of the neutral bases involved. Beyond this, however, it requires no knowledge of surface structure, area, pore size or any of the other quantities frequently considered in connection with the chemistry and physics of surfaces.

**Measurement of Acid Strengths.**—If this proposed definition of acid strength is applicable to surfaces, the acid strength of any surface should be readily measurable by observation of the color of suitable indicators adsorbed upon it, the appearance of the color of the acid form of the indicator indicating a value of the $H_0$ function for the surface lower than the $pK_a$ of the indicator employed.[5] Although this technique has been used in all the work reported here, it is subject to several restrictions which should be enumerated. First, as in the case of measurements in homogeneous media,[1] the indicators must be restricted to those in which the basic form is uncharged and, further, which are converted to their conjugate acids by simple proton addition. Second, they must be adsorbed by the surfaces under study (failure to adsorb available indicators made measurements on several materials impossible). Third, it is at least desirable that the acid form of the indicator be more highly (or noticeably differently) colored than the basic form, since adsorption might conceivably occur in layers, with a layer of indicator in its acid form (if it were colorless) masked by basic indicator overlying it. Fourth, the solvent from which the indicator is adsorbed may also be adsorbed on, and alter, the acid properties of the surface under study. This phenomenon will be considered in greater detail below, but, in order to minimize such effects, it has been found desirable to employ a non-polar solvent (generally isoöctane) as the medium for measurements. Fifth, simple visual comparison of the colors of adsorbed indicators as employed here, permits only a semi-quantitative determination of acid

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[1] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. IX.

[3] Braude and Stern, *J. Chem. Soc.*, 1982 (1948).

[4] Lewis and Bigeleisen, THIS JOURNAL, **65**, 1144 (1943).

[5] It should be recalled that *decreasing* values of $H_0$ indicate *increasing* acid strength.

strengths. More accurate measurement however is undoubtedly possible with more elaborate equipment. Finally, the indicator method is obviously limited to white or light-colored surfaces, although it might be extended by the use of fluorescent indicators. With these restrictions in mind, the indicators listed in Table I were chosen as covering a suitable range of acidities, the acid ionization constants ($pK_a$'s) of the anthraquinone and the dinitroazo compound being measured as part of this study.

TABLE I

INDICATORS FOR DETERMINATION OF SURFACE ACID STRENGTHS

| Indicator | Color change with acid | $pK_a$ |
|---|---|---|
| *p*-Dimethylaminoazobenzene | Yellow → red | 3.29[6] |
| 1,4-Di-(isopropylamino)-anthraquinone | Blue → red | 1.69 |
| Benzeneazodiphenylamine | Yellow → violet | 1.52[2] |
| *p*-Nitrobenzeneazo-(*p*'-nitro)-diphenylamine | Orange → violet | 0.43 |

For some of the more acid surfaces *o*-chloroaniline ($pK_a$ − 0.17) and *p*-chloro-*o*-nitroaniline ($pK_a$ − 0.91) were also employed, although, since their conjugate acids are colorless, they are less satisfactory.

## Experimental

**Indicators.**—*p*-Dimethylaminoazobenzene and benzeneazodiphenylamine were commercial indicators. The 1,4-di-(isopropylamino)-anthraquinone was a sample kindly supplied by Dr. M. S. Whelen of the Jackson Laboratory, E. I. du Pont de Nemours and Co., together with several other anthraquinone indicators. As well as the color change from blue to red it undergoes another change from red to colorless in very strongly acid solutions probably corresponding to the addition of a second proton to the molecule. *p*-Nitrobenzeneazo-(*p*'-nitro)-diphenylamine was prepared by coupling diazotized *p*-nitroaniline to *p*-nitrodiphenylamine in acetic acid solution. Coupling required several hours at room temperature, and the product, which crystallized from solution, was recrystallized from hot acetic acid. Its homogeneity was established by paper chromatography using benzene for development.

**Determination of indicator constants** was carried out in 90% acetic acid–water–sulfuric acid water mixtures by comparing the concentration of acid and base forms with those of indicators with known $pK_a$'s in the same solutions, essentially as described by Hammett and Deyrup for their work in sulfuric acid–water mixtures.[1] Concentrations were determined photometrically with a Beckman spectrophotometer using benzeneazodiphenylamine as the standard for the aminoanthraquinone, and *p*-nitroaniline for the *p*-nitrobenzeneazo-(*p*'-nitro)-diphenylamine.

**Materials studied** fell in general into two classes. First, for the purpose of a rapid survey, a number of chemicals were selected from the stock-room on the basis of availability, suitable physical form and possible interest, and tested without further treatment. Second, a number of materials known to have large active surfaces and frequent catalytic activity were selected and studied with more care. These were dehydrated at 200° and stored in desiccators, and included the samples of silica gel, alumina, silica–alumina catalyst, super-filtrol and florisil.

Four samples of silica gel were employed, two commercial samples, one Davco silica gel from the Davison Chemical Corp. and the other 88–200 mesh material from Eimer and Amend. Two samples were prepared by dehydrating Baker and Merck Reagent silicic acids, and the fifth (Prep. I) by dehydrating the silica gel obtained as an intermediate in preparing the silica–alumina catalyst described below.

Two samples of alumina were studied, one the ordinary Alorco drying agent from the Aluminum Ore Co., and the other Fisher Chromatographic grade.

Three samples of mixed silica–alumina were investigated, one (Prepn. II) prepared by precipitating 60 g. of commercial water glass with 500 cc. of distilled water and adding normal hydrochloric acid to *p*H 7. The mixture gelled in a few minutes, was stirred, filtered and resuspended and rewashed twice with 500 cc. of water. A small portion of the gel was then separated, washed once more, and dried three hours at 200° and overnight at 500°. This provided the sample of silica referred to above. The balance was stirred one-half hour with 3 g. of aluminum chloride hexahydrate in 200 cc. of water, filtered, stirred with an additional 3 g. of aluminum chloride hexahydrate and made just alkaline with ammonia. After filtration it was dried as above. This procedure parallels that described in a number of patents on the preparation of silica–alumina cracking catalysts. A second sample (Prepn. III) was prepared by diluting 100 g. of waterglass to 600 cc. and adding a 10% solution of aluminum chloride hexahydrate until the acidity reached *p*H 6 (approximately 300 cc.) and washing four times. This sample was also dried as described above. A third sample of silica–alumina was in the form of Socony-Vacuum bead form cracking catalyst, kindly supplied by Dr. C. M. Fontana of the Socony-Vacuum Laboratories and stated to contain approximately 9.5% $Al_2O_3$ and 90.5% $SiO_2$ on a dry basis, plus 1–2% water. It was ground to pass a 40-mesh screen before use.

**The Florisil** was $^{60}/_{100}$ mesh material obtained from the Floridin Co. and described by them as a synthetic magnesium silicate containing approximately 14.6% MgO, 83.9% $SiO_2$ and 1.5% $Na_2SO_4$. It was prepared by the reaction of magnesium sulfate and sodium silicate solutions, and, after drying, activated at about 650°.

**Super-Filtrol** was obtained from the Filtrol Corp. and is described by them as a bentonitic clay, activated by washing with mineral acid and containing 58.3% $SiO_2$, 15.3% $Al_2O_3$, small quantities of other metal oxides, and about 16% water. It also contains a small amount of sulfur, 0.34% as $SO_3$.

**Technique.**—Determination of surface acidity was in general made by placing about 0.2 cc. of the material to be tested in the form of a powder in a 10 × 75 mm. test-tube, adding 2 cc. of isoöctane (Phillips Petroleum Co. 99%) containing about 0.2 mg. of indicator and shaking briefly. Adsorption, if it occurred at all, was rapid and the color difference between acid and basic forms of the indicator striking.

## Results and Discussion

**Surface Acid Strengths of Various Surfaces.**—Materials found capable of adsorbing the indicators of Table I from isoöctane solution are listed in Table II, together with the colors of the adsorbed indicators. In addition the following chemicals were tested, but showed no adsorption, so no measurement could be made: $SnO_2$, $Hg_2Cl_2$, $PbCl_2$, $H_2MoO_4$, $Bi_2O_3$, $CaCO_3$, $H_3BO_3$, $ZnO_2$.

Table II permits the drawing of a number of important conclusions. First, although most of the adsorbents tested showed surface acidity, indicators are adsorbed either as neutral bases or as their conjugate acids. Thus, conversion to conjugate acid is not a requirement for adsorption, and the properties of adsorbing power and acidity

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(6) Guntelberg and Schiodt, *Z. physik. Chem.*, **135**, 393 (1928).

TABLE II

COLORS OF INDICATORS ADSORBED ON COMMON CHEMICALS

| Chemical | Color of indicator[a] | | | |
|---|---|---|---|---|
| | *p*-Dimethylaminoazobenzene | 1,4-Di-(isopropylamino-)anthraquinone | Benzeneazodiphenylamine | *p*-Nitrobenzeneazo-(*p*′-nitro)-diphenylamine |
| CaF | Y | B | .. | .. |
| $TiO_2$ | Y | B | .. | .. |
| $CaSO_4$ | R | .. | X | .. |
| $CaCl_2$ | R | X | Y-V | .. |
| CuCl | R | .. | Y-V | .. |
| AgCl | R | .. | Y-V | .. |
| $Sb_2O_5$ | R | R | V | O |
| $H_2WO_4$ | R | R | V | O |
| $Mg_2(ClO_4)_2$ | R | .. | V | O–V |
| $AgClO_4$ | R | .. | V | O–V |
| $Fe_2(SO_4)_3 \cdot xH_2O$ | R | R | V | X |
| $CuSO_4$ | R | R | V | V |

[a] B = blue, O = orange, R = red, V = violet, Y = yellow, X = no adsorption, Y-V, etc. = partial adsorption as conjugate acid, and an intermediate color.

are apparently independent. Second, the color of the adsorbed indicator is, in every case, that of the base or its conjugate acid as observed in homogeneous solution or intermediate between the two. This observation, which has been confirmed for a number of other mono- and disazo indicators, 1,4 diamino- and 1,4-dianilinoanthraquinone, 1,1-dianisylethylene and anisylacetophenone and *o*-nitroaniline, is evidence that we are here actually observing a base–conjugate acid conversion. Third, color changes parallel the indicator constants of the indicators employed, *i. e.*, in no case is an indicator adsorbed as the free base on a given surface when a more weakly basic indicator appears as its conjugate acid. This is a critical condition if our proposed definition of surface acidity is to have utility, and it is hoped to test it with a wider variety of indicator structures than the amino-azo and aminoanthraquinone configurations here employed.[7] Consideration of the relation between chemical structure and surface acid strengths among the chemicals of Table II is complicated by the possibility that some show anomalously high acidities due to mineral acids retained in their preparation, a difficulty which is considered at greater length in the next section. However, it may be noted that surface acid strengths parallel, to some extent, the ability of the metal ions to form coördination compounds by accepting electron pairs (iron, copper and silver ions are found on the strongly acid surfaces). Surface acidity here may thus represent not proton donation, but be a measure of the extent to which the coördinating ability of the metal ions is not bound up by the other components of the crystal lattice. Anhydrous copper sulfate is of particular interest, for not only does it adsorb all the indicators of Table II with the colors of their conjugate acids, but also *o*-nitroaniline ($pK_a$ − 0.17) in its colorless form. It fails to adsorb *p*-chloro-*o*-nitroaniline ($pK_a$ − 0.91) or *p*-nitrodiphenylamine ($pK_a$ − 2.38) so it may be concluded that on its surface $H_0 < \sim -0.5$.

**Surface Acid Strength of "Active" Surfaces.**—Investigation of the acid properties of materials with large surfaces, known to be active as adsorbents and frequently as catalysts, seems of particular interest. Results on a number of such materials, some obtained from several sources, are presented in Table III, and their identification is given in more detail in the Experimental part. A variation in surface acidity between different samples of silica gel is quite evident, and, since the first experiments were carried out using the Davco material, they suggested that silica surfaces were strongly acid. However, since a water extract of the Davco silica gel is acid (*p*H 3.25) and gives a precipitate with barium chloride, it seems likely that the material derives its acid properties from adsorbed sulfuric acid, a suspicion that is further confirmed by the observation that four washes with distilled water followed by drying give a product acid to *p*-dimethylaminoazobenzene but not to 1,4-di-(isopropylamino)-anthraquinone. Since an aqueous extract of the Eimer and Amend product is also acid (*p*H∼4) while the remaining three are neutral[8] it may be concluded that the surface of pure silica gel has a very low acidity.

TABLE III

ACID STRENGTHS OF SOME "ACTIVE" SURFACES

| Material | Indicator colors | | | |
|---|---|---|---|---|
| | *p*-Dimethylaminoazobenzene | 1,4-Di-(isopropylamino)-anthraquinone | Benzeneazodiphenylamine | *p*-Nitrobenzeneazo-(*p*′-nitro)-diphenylamine |
| Silica gel (Davco) | R | R | V | ... |
| Silica gel (E. & A.) | R | B–R | Y–V | ... |
| Silica gel (Baker) | Y | B | Y | ... |
| Silica gel (Merck) | Y | B | Y | ... |
| Silica gel (Prepn. I) | Y | B | Y | ... |
| Alumina (Alorco) | Y | B | Y | ... |
| Alumina (Fisher) | Y | B | Y | ... |
| $SiO_2 \cdot Al_2O_3$ (Prepn. II) | R | B–R | Y–V | O |
| $SiO_2 \cdot Al_2O_3$ (Prepn. III) | R | B–R | Y–N | O |
| $SiO_2 \cdot Al_2O_3$ (Soc. Vac.) | R | (B)–R | (Y)–V | O–(V) |
| $SiO_2 \cdot MgO$ (Florisil) | R | B–R | Y–V | O |
| Super-filtrol | R | R | V | V |

A similar retention of acid used in manufacture appears to account for at least some of the acid strength of the "Super-Filtrol" since it gives an acid extract with water and a precipitate with barium chloride. On the other hand, the other materials tested all give neutral extracts, so that the strong surface acid strengths of the hydrated silica–aluminas and silica–magnesia (between

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[7] It seems reasonable to expect that with indicators containing suitable chelating groups, surfaces containing certain metal ions will show anomalously high "acidities" and that the indicators may be adsorbed with quite different colors than those of their usual conjugate acids.

[8] The Baker material is stated by the manufacturer to contain only 0.02% $SO_4^{=}$ and 0.01% $Cl^{-}$.

that of 0.1 and 1.0 $N$ hydrochloric acid in water) are apparently real, and an intrinsic property of the materials. Since they contain quite firmly bound water, their surfaces may have the structure of "polyacids" of considerable strength.

**Effects of Concentration, Change of Solvent, etc.**—A possible complication in defining surface acid strength is that a surface might possess different regions of differing acid strength, so that if, for example, the more acid portions adsorb indicator more strongly, the apparent acid strength would decrease with the amount of indicator adsorbed. However, in none of the systems reported here in which the indicator constant of the indicator was near the acidity of the surface, so that the indicator was adsorbed in both its acid and basic forms, have we observed any change of hue with the amount of indicator added. Accordingly it appears that the surfaces studied are homogeneous, or that portions of different acidity adsorb at the same rate.

On the other hand, surface acid strengths do vary with the solvent with which they are in contact, as can be shown in the following way. If *p*-dimethylaminobenzene is adsorbed on Florisil from isoöctane, and acetone is added dropwise with shaking between drops the indicator is slowly eluted. In addition, however, the color of the indicator still adsorbed changes steadily from crimson through scarlet to orange. That this color change is not due to the yellow color of the solution is evident if Florisil to which the acid form of the indicator is adsorbed is viewed through the yellow solution, since its appearance is only slightly changed. Entirely similar results may be obtained with Socony–Vacuum catalyst colored by adsorbed benzeneazodiphenylamine. Here, as acetone is added, the color changes from violet through red to orange.

In some cases the amount of water bound by surfaces appears to affect their acid strength in a quite similar fashion. Florisil, freshly heated overnight at 600°, adsorbs benzeneazodiphenylamine to give a reddish-brown color indicative of partial conversion to the conjugate acid. Exposed to moist air until it has picked up 8% of its original weight of water, it adsorbs the same indicator as the yellow base, but still converts *p*-dimethylaminoazobenzene to its red conjugate acid. Similarly Socony–Vacuum catalyst, which freshly heated at 600° gives a red color with the weakest of the four indicators, *p*-nitrophenylazo-(*p'*-nitro)-diphenylamine, decreases in acidity on adsorbing 5.4% water and adsorbs the same indicator as its orange base and, in fact, only partially turns benzeneazodiphenylamine. That the adsorption of solvents having basic properties should decrease the acid strength of surfaces is certainly not surprising. It indicates, however, that in discussing surface acidity the dryness of the sample and the solvent with which it is in contact are important.

**Surface Acidity and Catalytic Properties.**—The concept of surfaces as reasonably strong acids, and a means of at least comparing the acid strengths of different surfaces suggests a new tool for the study of heterogeneous catalysis, which has, in general, been approached from quite a different point of view. In particular, it emphasizes the possibility that many examples of heterogeneous catalysis are, fundamentally, cases of acid catalysis occurring on an acid surface, an interpretation which, as far as the writer is aware, has received little general attention, but for which there appears to be considerable support in the literature.[9] Thus, we find that silica–alumina, silica–magnesia and acid-washed clays, all apparently strong surface acids, are among the effective cracking catalysts used in the petroleum industry, and the idea that this process, of such great technical importance, is one involving acid catalysis is supported by the fact that other cracking agents are aluminum chloride and phosphoric acid deposited on silica. Silica–alumina and the activated clays are also effective catalysts in bringing about acylation and alkylation of aromatic nuclei[10,11] and the isomerization and polymerization of olefins,[12] all reactions subject to acid catalysis in homogeneous systems. Incidentally, the properties of our Davco silica gel suggest that the rapid isomerization of 2,2,4-trimethyl-2-pentene and other olefins observed by Gallaway and Murray[13] over silica gel from the same source represent an acid-catalyzed reaction brought about, not by the silica surface itself, but by residual adsorbed mineral acid. Further examples of heterogeneous acid catalysis are provided by the ability of the acid form of cation exchange resins to promote acid-catalyzed reactions reported by Sussman,[14] and by Haskell and Hammett.[15]

A more complicated situation appears to be presented by the well known vapor phase catalysis by alumina and silica of such reactions as the dehydration of alcohols which are normally acid-catalyzed in solution. A possible explanation is that the rates of these reactions involve series of equilibria in which water is eliminated from the molecule, and the rate expressions thus involve the activity of water. If so, the catalytic effects of the silica and alumina may be derived from their abilities to adsorb and reduce the activity of water, rather than from their acid strengths.[16] An easy demonstration of the difference in be-

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[9] This point of view does appear to have gained some recognition among petroleum chemists. *Cf.* Thomas, *Ind. Eng. Chem.*, **41**, 2564 (1949); Greensfelder, Voge and Good, *ibid.*, **41**, 2573 (1949).

[10] Sachanen and Caesar, *ibid.*, **38**, 43 (1946).

[11] Hartough, Kosak and Sardella, THIS JOURNAL, **69**, 1014 (1947).

[12] Egloff in Chapt. I, Gilman, "Organic Chemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943.

[13] Gallaway and Murray, THIS JOURNAL, **70**, 2584 (1948).

[14] Sussman, *Ind. Eng. Chem.*, **38**, 1228 (1946).

[15] Haskell and Hammett, THIS JOURNAL, **71**, 1284 (1949).

[16] The analogous situation in homogeneous media has been discussed by Hammett.[2]

havior on adsorption on alumina or (pure) silica of materials which yield a conjugate acid by simple proton addition, and materials which undergo more complex ionization with loss of water (or another polar molecule), may be had by shaking alumina or silica with an isoöctane solution of the leuco base of malachite green, *p*,*p*'-bis-(dimethylamino)-triphenylcarbinol, adsorption occurring as the green dye. A whole series of similar color changes has been observed by Weitz and Schmidt,[17] although their results may be complicated by the fact that their silica, since it adsorbed *p*-dimethylaminoazobenzene as its red form, must have contained some free acid.

This difference in behavior toward two classes of indicator suggests the possibility of still further characterizing surfaces by observing the color changes occurring with both (*e. g.*, a series of simple bases, and a series of triphenylcarbinols) and in turn relating the results to their catalytic behavior.

## Summary

1. A definition of the acid strength of a solid surface is proposed as *the ability of the surface to convert an adsorbed neutral base as its conjugate acid.*

2. By observation of the colors of suitable adsorbed indicators the acid strengths of a number of materials have been semi-quantitatively determined.

3. Colors of the adsorbed indicators are, in every case, those of the indicator or its conjugate acid as observed in homogeneous solution. Further, acid strengths appear independent of the indicator employed, so the above definition appears a general and useful one.

4. Surface acid strengths depend somewhat upon the medium from which the indicator is adsorbed, and are decreased by the presence of weak bases, *e. g.*, acetone or water.

5. Although alumina and pure silica appear to have neutral surfaces, silica–alumina and silica–magnesia are strongly acid. Several surfaces containing strongly coördinating metal ions, *e. g.*, copper sulfate, silver chloride, etc., are also strongly acid.

6. The relation between surface acidity and certain examples of heterogeneous catalysis is discussed.

PASSAIC, NEW JERSEY RECEIVED OCTOBER 29, 1949

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[17] Weitz and Schmidt, *Ber.*, **72B**, 1740, 2099 (1939).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Heterogeneity of Catalyst Surfaces for Chemisorption. III. Metallic Nickel

BY HUSSEIN SADEK[1] AND HUGH S. TAYLOR

In earlier communications[2] the heterogeneity of oxide catalysts for chemisorption has been demonstrated by a new technique in which adsorption was measured under constant pressure at different temperatures without intermediate evacuation. In this communication we present the results of parallel investigations on a series of nickel catalysts to indicate that similar behavior occurs both with oxide and metal catalysts.

Benton and White[3] early showed that a distinct minimum in the adsorption isobar of hydrogen on metallic nickel occurs, interpretable as a change from van der Waals adsorption to chemisorption, in their experiments in the temperature region −190 to −100°. On this interpretation, the activated adsorption above −100° was a rapid process. The researches of Beeck and his coworkers[4] have indicated that on evaporated nickel films the processes of chemisorption were rapid and complete down to temperatures of liquid nitrogen. Eucken and Hunsmann,[5] working with reduced nickel catalysts, found that van der Waals adsorption with a heat of adsorption of ~1 kcal. occurred at liquid hydrogen temperatures; at 50°K. the heat of adsorption was indicative of a partial van der Waals adsorption and partial chemisorption, while at liquid-air temperatures and higher the process occurring was chemisorption with a heat of adsorption of ~20 kcal. By a desorption technique these authors indicated that the surface of their nickel was heterogeneous so far as the adsorption process for hydrogen was concerned.

The aim of the present investigation was to examine a series of nickel catalysts by the adsorption technique developed by Taylor and Liang to determine how far different methods of preparation might influence the temperature range in which van der Waals adsorption of hydrogen changed to chemisorption and to reveal, by this newer technique, the extent to which heterogeneity of the catalyst surface might be present in each case. The results of the adsorption experiments were checked in two cases by studies of the hydrogen–deuterium reaction on the catalysts.

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[1] This article is based upon a Thesis submitted by Hussein Sadek in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University, May, 1948.

[2] (a) Taylor and Liang, THIS JOURNAL, **69**, 1306, 2989 (1947); (b) Taylor, "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, Chap. 1, pp. 1–26.

[3] Benton and White, *ibid.*, **52**, 2325 (1930).

[4] Beeck, Smith and Wheeler, *Proc. Roy. Soc.* (*London*), **177A**, 62 (1940); Beeck, *Rev. Mod. Phys.*, **17**, 61 (1945).

[5] Eucken and Hunsmann, *Z. physik. Chem.*, **B64**, 163 (1939).