

SURFACE AREA OF CATALYSTS

Effect of Sintering on Area and Structure of a Supported Catalyst and Its Components

If the entire area of the catalyst is uniformly active and of the same relative accessibility, the relation between area and activity losses on heating is direct. If only active centers function, their extent in some cases may also be proportional to the total area. However, it is more likely that during the sintering process the fraction of such active centers that disappears is greater than the fraction of total area lost. A simple geometric relation may account in part for this if active centers exist in the form of edges and points and if sintering is considered to be the formation of larger particles or crystals. It has been pointed out (17) that for equal masses of geometrically similar particles the sum of the edge lengths is proportional to the square of the total surface, and the total number of points is proportional to the cube of the total area. Hence, if active centers are represented by edges and points, the activity of the catalyst may be very sensitive to area change on sintering.

Finally, area measurements may yield valuable information concerning the structure and function of supports. Careful investigation of the surface characteristics of the support should be accompanied by corresponding studies of the supported catalyst and the unsupported material.

The present paper deals principally with adsorption isotherm area measurements of a supported catalyst and its components. Included is a preliminary discussion of the high relative pressure region of the isotherms as related to hysteresis, average pore radii, and the number of adsorbate layers deposited at the saturation pressure.

DETERMINATION OF ADSORPTION ISOTHERMS

The apparatus and procedure are essentially the same as described by Emmett and Brunauer (5, 6, 8). Figure 1 is a general view of the two systems now in use. Each apparatus includes a 100-cc. bulb buret, a 5-cc. buret-manometer graduated in 0.01-cc. units, a mercury diffusion pump system, a McLeod gage, and a vapor pressure thermometer. Reservoirs and purification trains for nitrogen and helium are also incorporated.

An oxygen vapor pressure thermometer is used for low-temperature measurement in the following studies. The nitrogen vapor pressure values for relative pressure calculations are obtained from an experimentally determined curve of nitrogen vapor pressure vs. oxygen vapor pressure thermometer readings. The temperatures of the liquid nitrogen bath are then obtained from these data using the values determined by Keesom and Bijl (14).

During the portion of the isotherm determination used for calculating area by the Brunauer-Emmett-Teller (BET) method (3), the temperature of the liquid nitrogen bath rarely varies more than 0.03° C. as measured by the oxygen vapor pressure thermometer. The range of liquid nitrogen temperature variation for different experiments is somewhat greater, approximately 0.4° C. It was found experimentally that the use of relative pressures corrects satisfactorily for temperature variation in this range. In some of the long time-interval determinations necessary to obtain equilibrium data in the high relative pressure region, temperature variation is somewhat greater than in the BET portion. However, the frequent addition of liquid nitrogen somewhat richer in nitrogen than the original bath is effective in maintaining relative constancy over periods of several days.

The nitrogen and helium gases used in these experiments are obtained from the Ohio Chemical Company and are, respectively, 99.8 and 98.2% pure. The nitrogen is further purified by copper gauze at 500° C., a large drying tube containing barium oxide or phosphorus pentoxide, and a dry ice-acetone trap. The helium is further purified with activated charcoal packed in a trap at liquid nitrogen temperatures. The purifications are performed batchwise by allowing small volumes of the gas to remain in the purification system approximately 30 minutes.

The supported catalyst, A, is in the form of 1/8-inch pellets. The unsupported catalyst, B, was prepared by L. E. Olson of

THE IMPORTANCE of surface area measurements in catalyst studies is discussed. Nitrogen adsorption isotherms are used to follow area changes of a supported catalyst after heating for various periods at 340°, 400°, 500°, 600°, and 650° C. Similarly, area values are obtained for the diatomaceous earth support after 340° and 650° C. heat treatments and for the unsupported catalyst after a 340° treatment. Areas calculated according to the Brunauer-Emmett-Teller equation show that the supported catalyst has a considerably greater area than either the unsupported material or the support. The supported catalyst loses 5% of its area at 500° C., 26% at 600°, and 75% at 650°; the support suffers a loss of 39% at 650° C. Fair agreement is found between the measured area of the support and the area of a model based on electron microscope pictures. An adsorption-desorption isotherm determination on the supported catalyst demonstrates a pronounced hysteresis effect which is discussed in relation to pore structure. Consideration is also given V_a/V_m isotherms as a means for studying specificity in nitrogen adsorption on the various solids.

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these laboratories in a manner similar to that used for the supported catalyst. Catalyst B is in the powder form. The carrier, support C, is a finely divided diatomaceous earth.

Each isotherm determination is preceded by a thorough degassing of the catalyst and adsorption bulb in an overnight elevated-temperature evacuation. The catalyst sample is maintained at 340° C. and 10⁻⁶ mm. pressure for approximately 16 hours. Some of the sintering treatments are accomplished at higher temperatures during this evacuation, but in all other experiments the 340° C. evacuation is standard procedure. The sintering treatments are performed in vacuo for temperatures up to and including 500° C. At 600° and 650° C. the catalyst is heated in helium at atmospheric pressure in order to prevent distortion or collapse of the relatively thin-walled Pyrex adsorption bulb.

Dead-space volumes may be measured with helium at liquid nitrogen temperatures or with nitrogen or helium at room temperature. According to Emmett (7), nitrogen may be adsorbed at room temperature and atmospheric pressure to the extent of

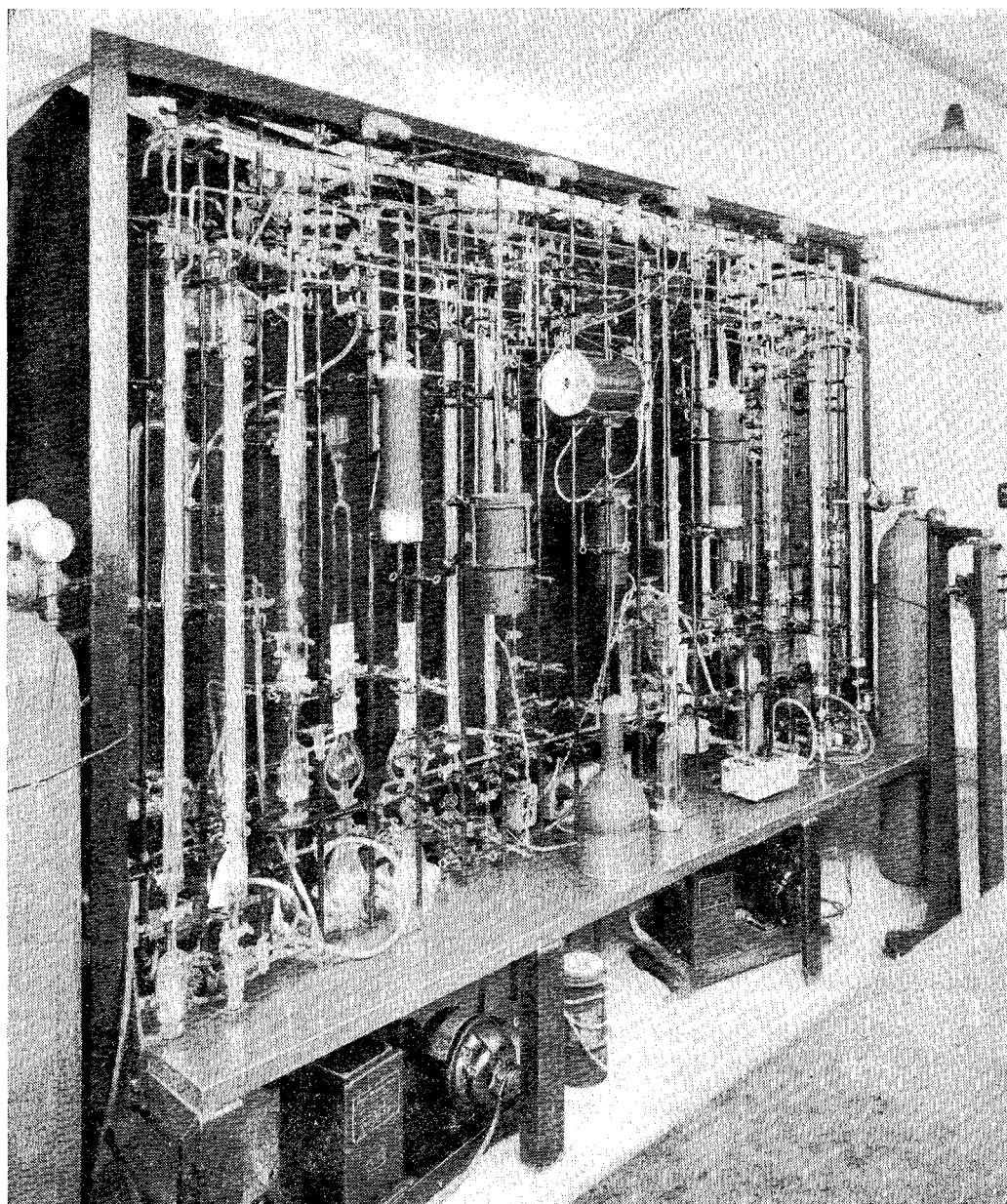


Figure 1. Adsorption Isotherm System for Catalyst Studies

0.02 fraction of a monolayer. Adsorption of nitrogen at room temperature thus introduces an error in the nitrogen dead-space measurement. The magnitude of the resulting inaccuracy in the adsorption data, however, varies throughout the isotherm since the amounts of gas adsorbed and held in the dead space are different functions of the pressure. Consequently the use of helium is generally preferable. The measurement with helium is conveniently performed under conditions corresponding to those of the isotherm experiments; that is, the catalyst bulb is immersed in liquid nitrogen during the determination. The volume of nitrogen adsorbate in the dead space is corrected for the deviation of nitrogen from the perfect gas law. The correction is based on a 5% deviation at -195.8°C . and 760 mm., with an assumed proportional variation with pressure as recommended by Emmett and Brunauer (9).

In the present study the dead-space volumes are obtained by means of nitrogen at room temperature, with the exception of experiments 33 and 34 in which helium is used at the temperature of the liquid nitrogen bath. Dead-space measurements, how-

ever, have been performed with both helium and nitrogen for solids of the type studied here. These experiments demonstrate that the error introduced in the area measurements may be as great as 1%. In all cases in which nitrogen is used for the dead-space measurement it remains in the system as the first addition of adsorbate gas, and therefore adsorption at room temperature does not enter as a double error (dead space and volume adsorbed). Another factor that must eventually be considered in a rigorous treatment of dead space is the reduction of the dead space by the volume of the adsorbed material.

A somewhat qualitative statement may be made at this point regarding the time required for adsorption equilibrium. In the relatively linear central portion of the common sigmoid isotherm, equilibrium is reached quite rapidly. For points on the steeply rising initial portion of the curve, equilibrium is achieved in a slightly longer period for similar pressure increments. Considerably greater time is re-

quired in the higher relative pressure portion of the isotherm. Near the saturation pressure in the following series of isotherms, time intervals of 2-4 hours may be required to establish equilibrium.

It may be that the equilibrium time is related to the time required for the dissipation of the heat liberated on adsorption and is, consequently, a function of the amount adsorbed and the heat of adsorption. Heat liberated at the catalyst surface is difficult to dissipate in the finely divided solid, low-pressure gas system, as pointed out by Beebe (1). Large amounts of gas are adsorbed for small pressure increments at the relatively low pressures. Similarly, large volumes are adsorbed or condensed in capillaries in the high-pressure region. However, in the linear central portion small volumes are adsorbed for corresponding pressure increments; also the heat of adsorption is less for the second layer than for the first. These relations are apparently in good agreement with the observations.

The extremely slow equilibration in the higher relative pressure region, requiring 2-4 hours near the saturation pressure, may be due, however, to several factors. For example, the decrease

in the effective pore radii by the thick films deposited in this region will decrease the rate of gas diffusion to the interior and will retard the movement or distillation of condensed adsorbate into equilibrium positions in the capillaries. This factor combined with the thermal effects of adsorption-condensation phenomena may account for some of the equilibrium difficulties.

CALCULATION OF AREA

Area values are calculated from the adsorption isotherms by means of the Brunauer-Emmett-Teller (BET) equation (3):

$$\frac{p}{V_a(p_0 - p)} = \frac{1}{V_m c} + \frac{(c-1)p}{V_m c p_0}$$

where V_a = volume adsorbed at measured pressure, p ; V_m = volume adsorbed in monolayer; p_0 = saturation pressure of adsorbate gas; c = a constant related to heat of adsorption and heat of condensation of adsorbate.

Since the equation is linear, a plot of $p/V_a(p_0 - p)$ against p/p_0 will yield a value for V_m . The least squares method is applied to the following data.

Emmett and Brunauer suggest using the linear portion of such a plot between 0.05 and 0.35 relative pressure. The data of most

of the following experiments fall on good straight lines over a slightly smaller range. Near 0.05 relative pressure the deviations are almost negligible, but at 0.30 relative pressure they become appreciable in a number of experiments. The deviations are always below the line at 0.05 and above at 0.35 relative pressure (Figure 5). Consequently, the data are used up to the point at which the expected trend in the deviations appears.

Each area value has been confirmed by at least one duplicate determination. It is convenient and practically necessary, particularly for the *in situ* sintering studies, to express area as area per gram of the original weight of the catalyst, although it is recognized that volatile matter may be lost during sintering treatments. Similarly V_a and V_m represent volumes adsorbed per gram of original weight.

The V_m values obtained by the BET method are translated into area units (square meters per gram) by using 16.2 sq. Å. as the area value for the nitrogen molecule (9). Harkins and Jura (12), however, suggest the use of 15.25 sq. Å. for porous solids and 16.2 sq. Å. for nonporous solids. The V_m values are included in Table I because they represent relative areas according to the BET equation without the assumption of a specific molecular area for nitrogen; or more correctly, they represent the relative numbers of molecules adsorbed.

Table I brings out the good agreement between the calculated V_m values and those obtained from estimates of the B point, the lower extremity of the central linear portion of the isotherm, as recommended in the earlier work of Emmett and Brunauer (9). Careful examination of the so-called central linear portions of these isotherms reveals irregularities similar to a few cases reported by Emmett and DeWitt (10). Perhaps these are related to the phase changes now being studied by Harkins and Jura.

The last column of Table I gives the relative pressures corresponding to the V_m values. These are quite different for the various adsorbents listed. This difference may indicate an appreciable specificity in the adsorption and will be discussed further in connection with the isotherms plotted as adsorption per unit surface.

SINTERING

Because of the war a considerable portion of the results obtained may not now be disclosed. This discussion therefore represents only a small part of a rather extensive study of catalysts subjected to various treatments. The nitrogen isotherms for the series of sintered samples of catalyst A are presented in Figure 2. The decrease in adsorbing surface with increase in sintering temperature is apparent. Table I gives the calculated area values. The area of the original material, evacuated at 340° C., is taken as that of experiment 15, 119.8 sq. meters per gram; this value nearly represents the average of four determinations, three of which were performed on different samples in the adsorption bulb. The sample used in experiment 15 is relatively large, 4.997 grams, for a material in this area range.

The high relative pressure points near p_0 were determined in many of these experiments but are omitted in Figure 2. Figure 7 includes complete curves for those determinations in which special care was exercised in the high-pressure region. Figure 3 presents the isotherm data plotted according to the BET equation for the relative pressure range, 0.05 to 0.35.

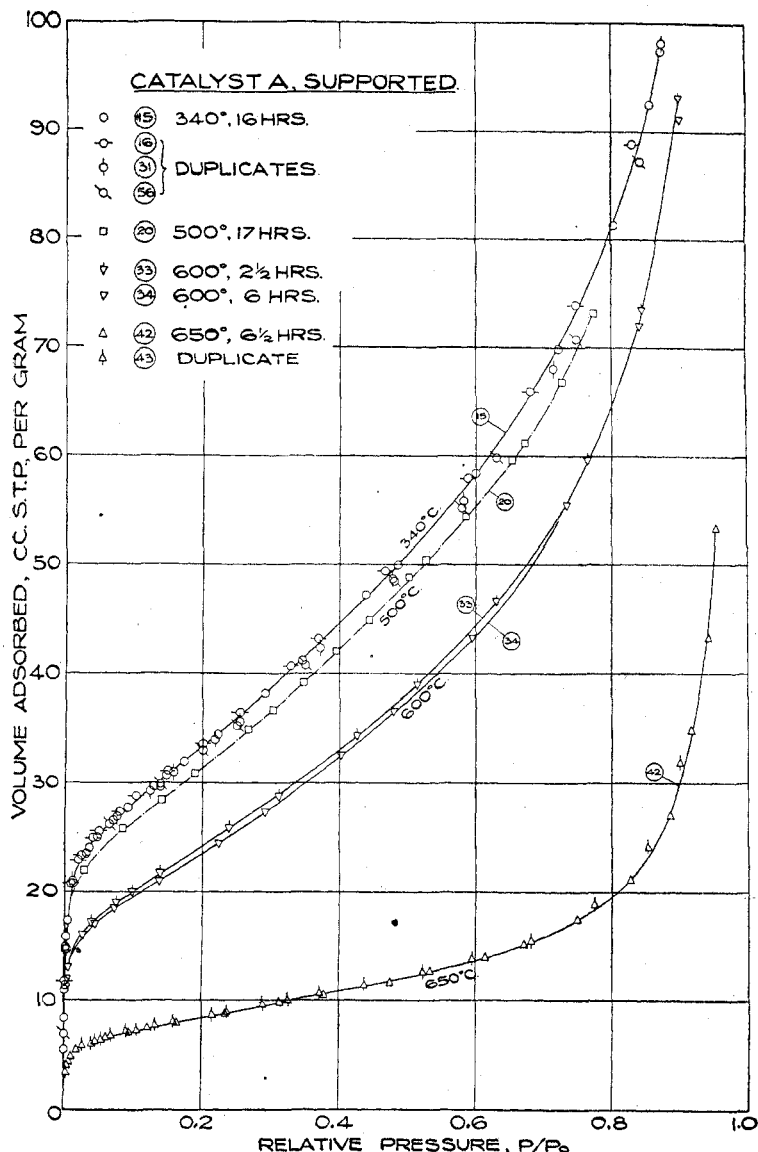


Figure 2. Nitrogen Adsorption Isotherms for Catalyst A, Supported

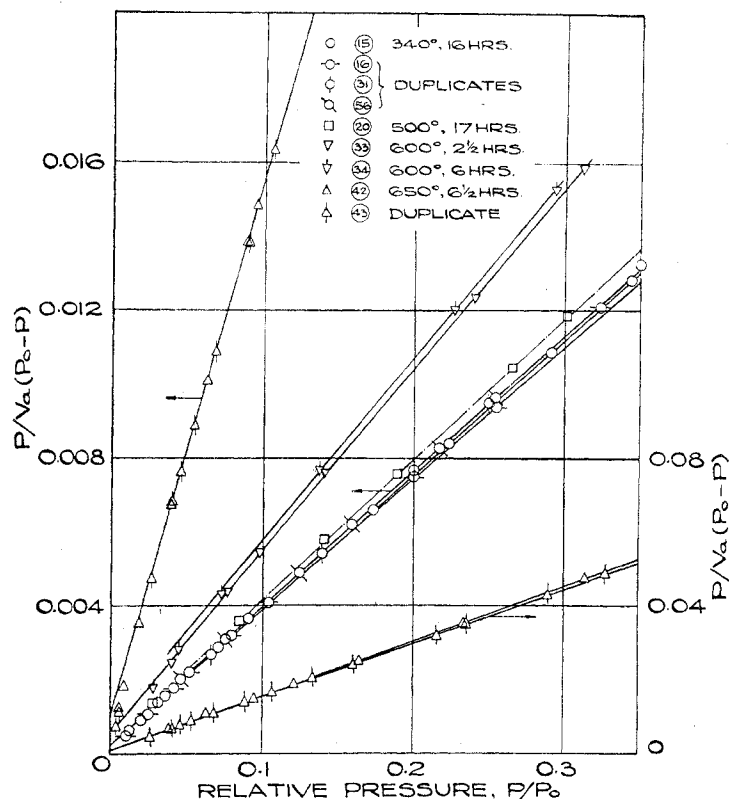


Figure 3. Nitrogen Adsorption According to BET Equation for Catalyst A, Supported

Although sintering experiments have been performed at 400° and 500° C., the detailed results are not included here as the conditions were not strictly comparable to those at 340°, 600°, and 650° C. Nevertheless, these closely related experiments indicate that no area loss occurs during the 20-hour treatment at 400° C. and that an area decrease of only 5% takes place when the catalyst is subjected to 500° C. for 17 hours. The 500° C. isotherms are the broken line curves in Figures 2 and 3.

At 600° C. the first 2.5-hour period of heating results in a considerable loss in area. This treatment is accomplished in helium at atmospheric pressure to prevent adsorption bulb collapse. The area decreases from the original value of 119.8 to 88.9 sq. meters per gram, a loss of approximately 26%. An additional heat treatment for 3.5 hours at the same temperature causes very slight further sintering, the isotherm giving an area of 88.1 sq. meters per gram.

On heating the catalyst at 650° C. for 6.5 hours in helium, the area falls to 29.5 sq. meters per gram. This represents a loss of 75% of the original area. A major collapse of the high surface area structure has evidently taken place.

UNSUPPORTED CATALYST AND SUPPORT

It is of considerable interest that the area of the supported catalyst is much greater than that based on additivity of the areas of its components. Isotherms for catalyst B, the unsupported catalyst, and for support C after 340° C. evacuations are plotted in Figure 4. Included in addition are isotherms for the original and the 650° C. sintered samples of the supported catalyst

and for the support sintered at 650° C. The data are plotted according to the BET equation in Figure 5. Deviations from the linear relation as described above are apparent.

Duplicate determinations of the unsupported catalyst area give 53.5 and 53.2 sq. meters per gram. These area values are considerably smaller than that of the supported catalyst, 119.8 sq. meters. The area of the support is 20.7 sq. meters per gram and decreases considerably on sintering at 650° C. for 6 hours, falling to 12.7 sq. meters, a loss of approximately 39%. Diatomaceous earth may contain a small amount of clay that contributes significantly to the support area. Sintering of the clay component may be responsible for some of the total area loss. Although this 39% loss is considerably less than the 75% loss in area suffered by the supported catalyst when subjected to the same treatment, it is recognized that such a change in the support surface structure may critically affect the catalyst superstructure. Preliminary sintering experiments with the unsupported material indicate that it loses approximately 60% of its area at 500° C. and that its surface may be very sensitive to temperature below 500° C.

The high area of the supported catalyst is remarkable when the relatively low areas of its components are considered. Supported catalysts of similar composition having almost twice the area reported here have subsequently been prepared. Obviously simple thin-film deposition on the surface of the low area support cannot account for the catalyst area. Careful study of the physical structure of the diatomaceous support may contribute to the understanding of its function in the high area catalyst. Nevertheless, in spite of the inert nature of diatomaceous earth, its weak chemical properties should not be entirely neglected.

Electron microscope pictures of diatomaceous earth reveal that the disk-type diatom skeleton may consist of a network of circular holes about 2000 Å. in diameter. Since the support material studied here contains a considerable portion of the disk type, it is of interest to estimate the surface area of such a structure. A model having contiguous circular cylindrical pores 2000 Å. in diameter and a solid density of 2.2 grams per cc., gives by simple geometry an area of 34 sq. meters per gram. This is of the same order of magnitude as the isotherm area, 20.7 sq. meters. Contiguous pores, 3200 Å. in diameter, in such a model will account for an area of 21 sq. meters per gram. Also, pores 2000 Å.

Table I. Nitrogen Adsorption Isotherm Data

Expt. No.	Treatment of Adsorbent			Area, Sq. M. per G.	% of Original Area	V_m , Co. Adsorbed in Monolayer on 1 G. Adsorbent	V_m Estd. by B. Point Method	p/p_0 Corresponding to V_m
	° C.	Hr.	Atm.	Grams				
Catalyst A, Supported								
15	340	16	Vacuum	4.997	119.8	100	27.52	26
20	500 ^a	17	Vacuum	4.997	113.5	94.7	26.08	25
22	500 ^a	33	Vacuum	4.997	113.3	94.6	26.03	..
33	600	2.5	Helium	1.994	88.9	74.2	20.41	20
34	600	6	Helium	1.994	88.1	73.5	20.23	19
42	650	6.5	Helium	2.009	29.5	24.6	6.78	7
43	650	6.5	Helium	2.009	29.9	25.0	6.87	..
Support C								
57	340	16	Vacuum	8.284	20.7	100	4.76	..
58	340	32	Vacuum	8.284	20.6	99.5	4.74	5
59	650	6	Helium	8.284	12.7	61.4	2.93	..
60	650	6	Helium	8.284	12.8	61.6	2.94	3.5
Catalyst B, Unsupported ^b								
69	340	16	Vacuum	2.305	53.5	...	12.28	12
70	340	32	Vacuum	2.305	53.2	...	12.23	..

^a Sintering treatments at 500° C. are not strictly comparable to those at other temperatures.

^b Prepared to resemble catalyst A without support C.

in diameter, separated by approximately 120 Å., would give an area value of 21 sq. meters. If 2000 Å. represents the pore center-to-center distance, a pore diameter of 1860 Å. and a pore separation of 140 Å. will yield an area of 21 sq. meters per gram. The latter models are more acceptable as they satisfy the electron microscope data and the need for solid partitions between adjacent pores.

If such relatively large pores are an essential characteristic of a good support for high-area catalysts of certain types, then, contrary to many current concepts, the need for a comparatively low-area porous carrier follows directly. Perhaps the large pores of the support may be responsible for the stable high-area structure of the catalyst. Catalyst deposition from solution should take place readily within such pores whereas the poor accessibility of the smaller pores in high-area support materials may prevent the formation of high-area catalytically active structures. Thus for a given catalyst there may be a support of optimum pore size.

ADSORPTION PER UNIT SURFACE

Brief reference has been made to the apparent similarity of the ordinary isotherms for the different adsorbents studied. How-

ever, appreciable differences in the relative pressures corresponding to the V_m values for these adsorbents are evident in Table I. Similarities and differences in adsorption characteristics are demonstrated more clearly by reducing the adsorption isotherms to unit adsorbent surface. Figure 6 presents the V_a/V_m isotherms; the differences in nitrogen adsorption per unit surface indicate different adsorption forces or interaction energies, provided pores are sufficiently large so that their structure does not affect the isotherms in the low-pressure range considered.

According to these isotherm plots, considerable specificity is associated with the low-temperature van der Waals adsorption on the various solids. In the low-pressure range where pore structure probably exerts a minor effect, the V_a/V_m isotherm of the support appears quite different from that of the supported catalyst. Of interest also are the differences between the supported catalyst and the same material sintered at 600° and 650° C. Adsorption characteristics of the unsupported catalyst appear somewhat similar to those of the supported catalyst.

Detailed interpretation must await further work. It is conceivable, however, that isotherms reduced to unit surface may eventually provide a means for differentiating and classifying solid surface types and structures.

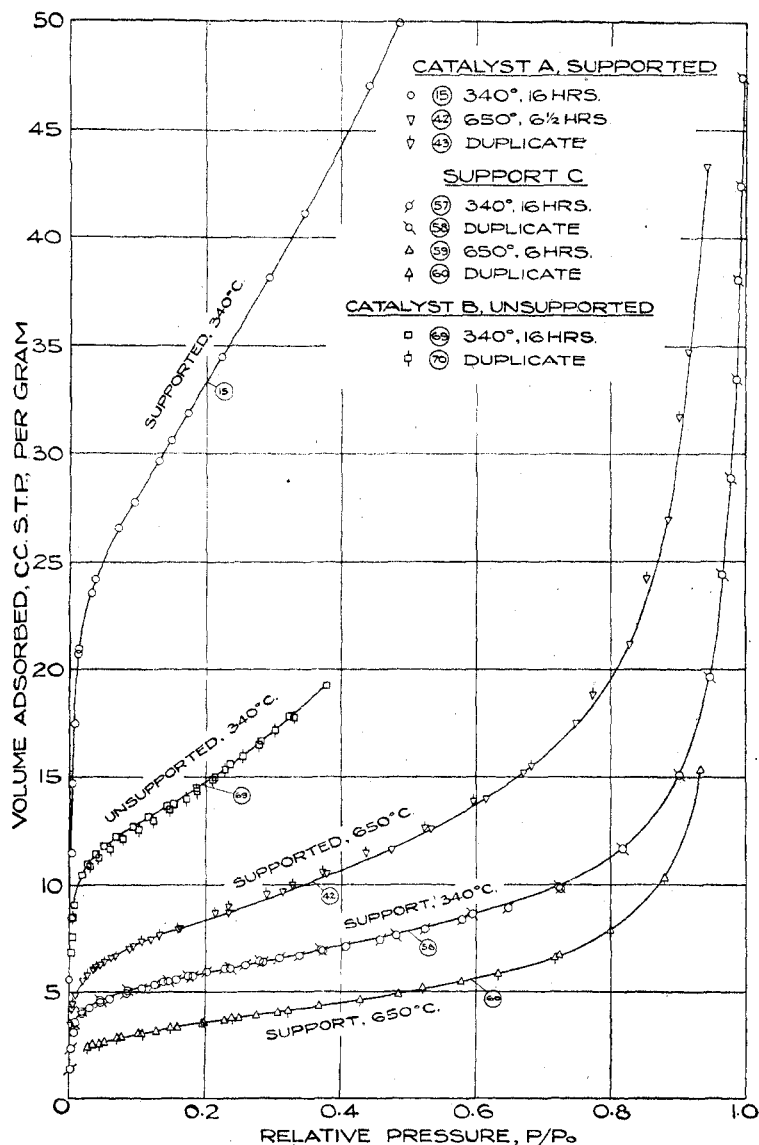


Figure 4. Nitrogen Adsorption Isotherms for Unsupported Catalyst B and Support C

HIGH RELATIVE-PRESSURE REGION AND PORE STRUCTURE

Careful study of the high relative-pressure region should yield additional valuable information concerning the surfaces of catalysts and supports. Considerable care has been exercised in obtaining equilibrium values for the higher pressure points plotted in Figure 7. Isotherms for three adsorbents are shown: the original supported catalyst, the 650° C. sintered sample, and the diatomaceous earth support. Two to four hours may be required for equilibrium readings in the upper portions of these isotherms.

The isotherms for the three adsorbents of Figure 7 approach p_0 asymptotically. They are type II isotherms according to the classification of Brunauer, Deming, Deming, and Teller (2, 5). The asymptotic approach, combined with the gradual curvature that precedes it, indicates a rather wide distribution of pore radii. The term "pore" as used here includes any internal space which may be in the form of cracks, crevices, or the interstitial space in a thin platelet structure. The three isotherms have no steeply rising portions followed by plateaus near p_0 , such as are typical for those porous adsorbents which possess a certain uniformity of pore radii and which give type IV isotherms. Evidently the materials whose isotherms are shown in Figure 7 possess some large pores that do not fill completely below p_0 . Adsorbents having extremely small pores of rather uniform radii might be expected to give the Langmuir type of flat isotherm, type I, since the pores fill almost completely at a relatively low pressure. Certain high-area carbons give this Langmuir type of isotherm.

An approximate thickness of the adsorbate film at p_0 in terms of the number of adsorbed molecular layers may be obtained by dividing the volume adsorbed at the saturation pressure, V_s , by the volume of the monolayer, V_m . The V_s volume is, at best, an approximation for the type of isotherm obtained in these studies since the approach to p_0 is asymptotic. Estimates of film thickness by this method give values quite different for the three materials whose upper isotherms were determined:

the supported catalyst, ten layers; the 650° C. sintered catalyst, thirty layers; and the support, about fifteen layers. The V_s/V_m values considered in making the above estimates are, respectively: 9.4, 10.8; 30.2, 33.6, 30.0, and 15.4, 17.2. For adsorbents having platelet structures of nonuniform wall separation, these values represent average adsorbate film thicknesses. Although it is clear that the number of layers on plane surfaces is represented by V_s/V_m , on concave (pore) surfaces the number of layers is greater and on convex surfaces the number of layers less than the V_s/V_m value. This variation with radius of curvature is due simply to the change in the volume of adsorbate required for a monolayer as the effective surface becomes greater or less with increasing adsorption.

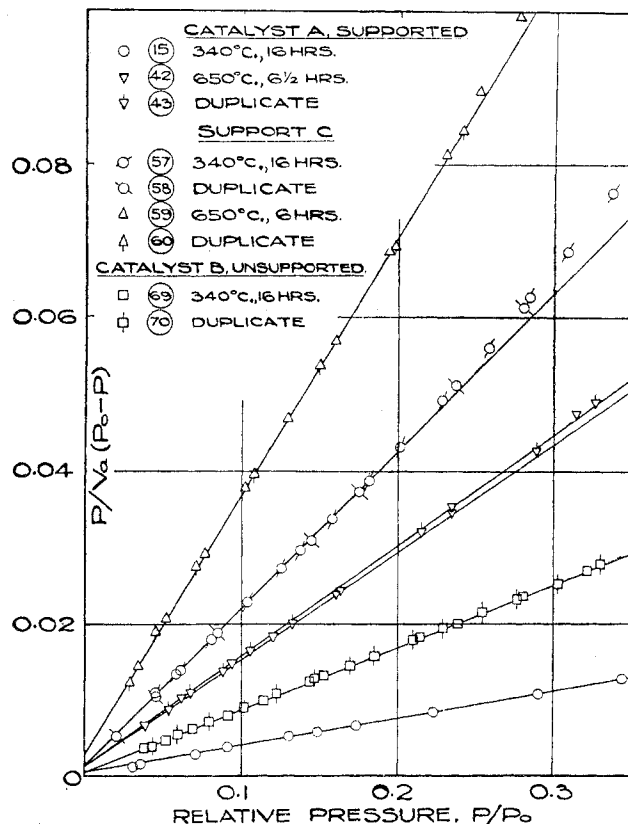


Figure 5. Nitrogen Adsorption According to BET Equation for Unsupported Catalyst B and Support C

The increase from ten to thirty adsorbate layers on sintering is probably associated with the increase in pore radii or platelet separation accompanying area loss. The area falls from 119.8 to 29.5 sq. meters per gram on sintering at 650° C. To account for the increased film thickness on the basis of a greater porosity would require a major porosity increase. Actually a decrease in porosity on sintering is indicated by the lower V_a value at p_0 (Figure 7). Direct helium-mercury displacement measurements of porosity by H. O. Bauermeister of these laboratories also show a decrease. Growth of average pore size is easily visualized if sintering is considered simply a crystal growth process in a pellet of constant volume and porosity. The pore spaces will effectively merge as do the solid particles or platelets.

One is tempted to attach significance to the number of layers deposited on an adsorbent as indicating the adsorptive forces of the solid; certainly thirty layers is an unusually large number of layers. However, the complicating factors of pore volume, pore radii, and capillary condensation make interpretation difficult for porous materials. Furthermore, since the approach to p_0 is asymptotic, the V_a value from which the number of layers is cal-

culated in each case is necessarily of preliminary interest only. The development of a better method for obtaining V_a is now in progress.

Emmett and DeWitt (11) pointed out the following simple inverse relation between pore radius r and surface area A for a high-area material with constant pore volume, V , and uniform cylindrical pores:

$$V/A = r/2$$

The same relation obtains for thin platelet structures with r as the platelet separation. The threefold increase in film thickness on sintering may correspond approximately to an increase in pore radius or platelet separation and bears a somewhat similar relation to the fourfold decrease in area.

The supported catalyst on heating at sintering temperatures probably approaches the large pore structure of the support. If the pore radii of the active catalyst material increase, it may be that some interesting increases in catalyst activity on sintering should be attributed to the greater accessibility of the larger pores. The smaller pores of the higher-area material may not admit large reactant molecules.

HYSTERESIS

The pore radius problem may be approached from an entirely different viewpoint by a consideration of the hysteresis effect. An adsorption-desorption isotherm for the original supported catalyst is shown in Figure 7. The hysteresis effect is quite marked. This experiment extended over a period of 4 days, and 4-8 hours were allowed for equilibration at the important points. If several hours are not allowed for equilibrium in the high relative-pressure region, one may easily observe a false hysteresis effect. The adsorption branch of the curve is displaced to the right by premature readings, and the desorption curve is displaced to the left. Nonequilibrium values thus exert a double effect on the widening of the hysteresis loop. Because of certain experimental difficulties inherent in long time-interval studies of the high relative-pressure region, it is possible that the 4-8 hour readings reported here may not represent true equilibria. Thus, the possibility that the hysteresis effect diminishes or even disappears as an equilibrium phenomenon is not excluded by these experiments.

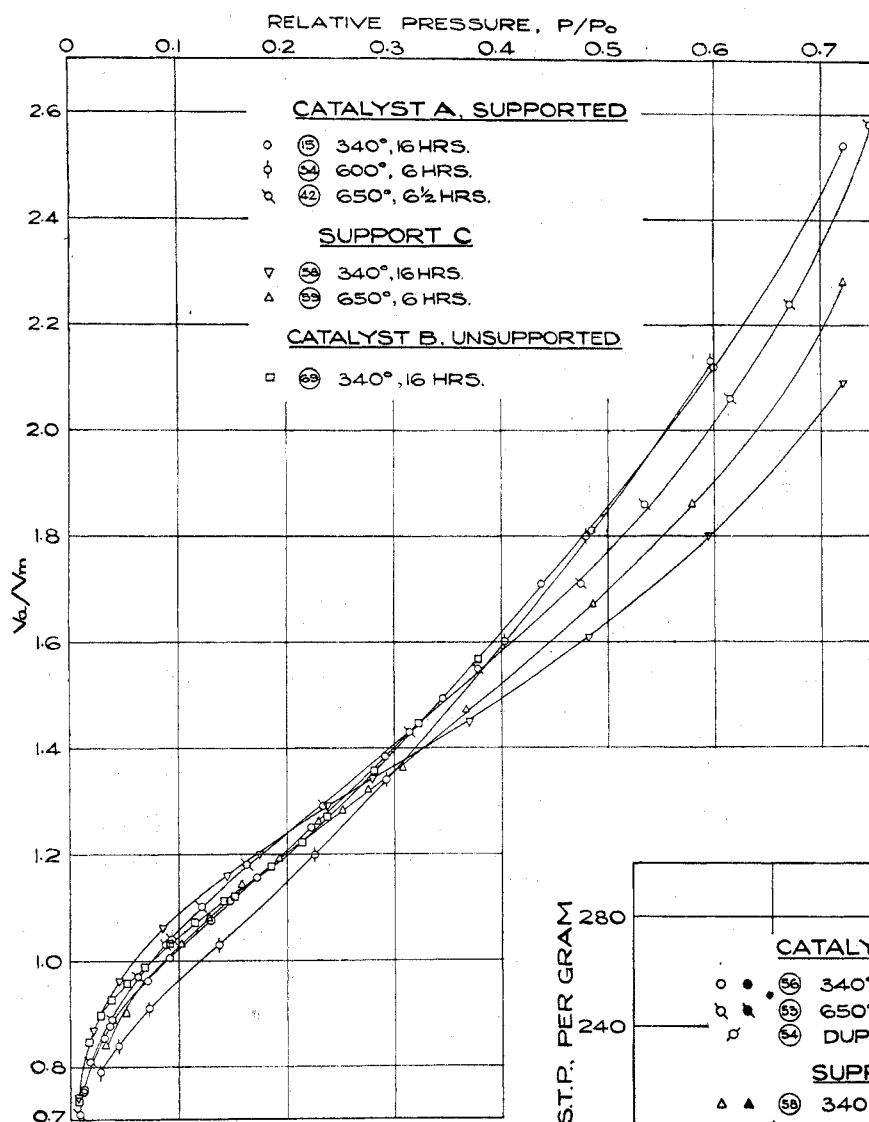
According to the simple bottleneck picture (15, 16) of pore structure as related to hysteresis, the wider the hysteresis loop, the greater the difference between the radius of the body of the average pore and the radius of its capillary neck. The bottleneck theory may be particularly applicable to certain types of pelleted materials because of the mechanics of pelleting. The pelleting process probably produces pores of smaller diameter at the surface than in the interior. Application of the Kelvin equation,

$$\ln p/p_0 = -2V\sigma/rRT$$

to the desorption branch of the hysteresis loop for the unsintered catalyst gives a value of approximately 13 Å. for the radius of the pore orifices emptying at 0.5 relative pressure. V is the volume of one mole of the liquid (nitrogen), σ its surface tension, r the capillary radius, R the gas constant, T the absolute temperature, and p the equilibrium pressure. This equation is used by Cohan (4) for desorption but is somewhat modified for adsorption. The relative pressure of 0.5 used in the above calculation corresponds to the approximate mid-point of the steepest part of the desorption branch. It would obviously be difficult to select a corresponding point on the adsorption branch of this type of isotherm.

The bottleneck radius thus calculated from the desorption curve may be more valuable in catalytic studies than the radius of the body of the pore obtained from the adsorption branch, if the former value represents an average radius of the pore orifices through which reactants must pass to reach the internal surface and through which products must be removed. The capillary pore orifice may be a controlling factor in the accessibility of the

Figure 6. Isotherms of Nitrogen Adsorption per Unit Surface



large internal surface of high-area catalysts. Furthermore, the outer portion of the pore or the pore neck may be important, per se, in that it may provide the only portion of the pore surface effective in certain catalytic reactions. Fundamental studies along this and related lines should prove valuable in the investigation of catalytic processes.

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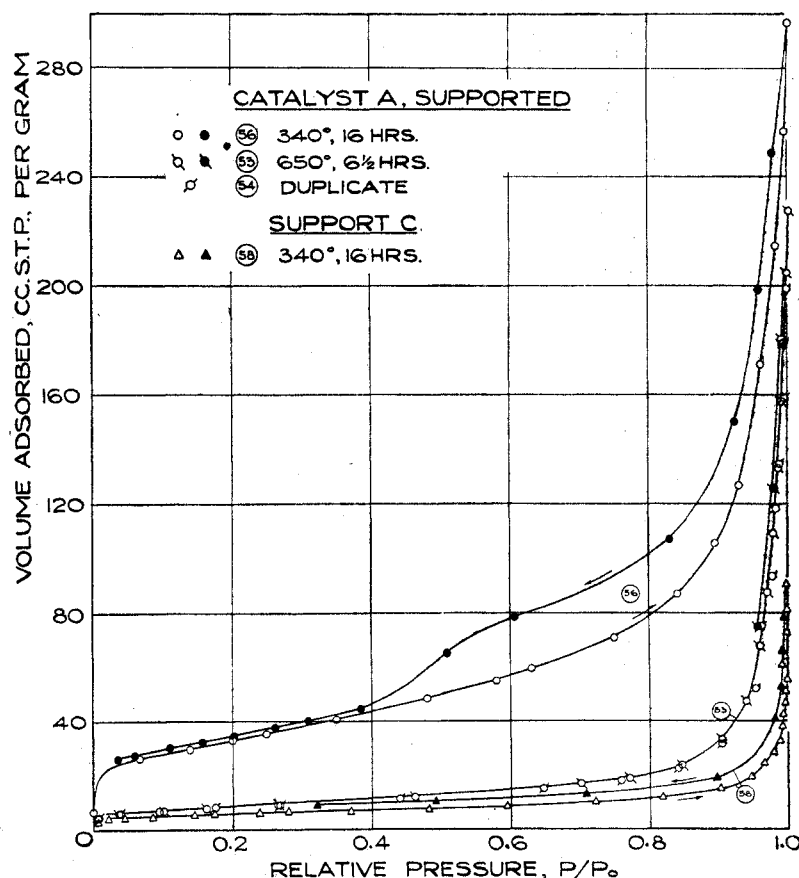


Figure 7. Isotherms for Nitrogen Adsorption and Desorption

IN CATALYTIC CRACKING, both fixed-bed and fluid, it has been found that there is an intrinsic uniformity in the way the carbon deposit on the catalyst increases with the time elapsed since the catalyst was last regenerated. For all the data examined, the amount of carbon deposited on the catalyst at given conditions is, within limits, inde-

pendent of the hydrocarbon feed rate. From this study, correlations are derived that define mathematically the interdependence between feed stock conversion, feed rate, and length of period between catalyst regenerations. A speculative hypothesis is advanced as a possible explanation of the mechanism of carbon formation.

CARBON FORMATION IN CATALYTIC CRACKING

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WHEN petroleum hydrocarbons undergo deep-seated reactions in the presence of solid catalysts, carbonaceous deposits usually accumulate on the catalyst and decrease its activity, so that periodic regeneration is necessary. A conspicuous exception is the case of high-pressure catalytic hydrogenation where the catalyst retains its activity for periods up to a year and longer without any regeneration (2). Examples of regenerative processes are (a) catalytic cracking of gas oils and (b) catalytic reforming of naphthas. This paper presents a discussion of certain aspects of the formation of carbonaceous deposits in catalytic cracking.

The carbonaceous deposit that is an inevitable by-product of catalytic cracking is called "coke", and is generally determined as the weight per cent of carbon on feed or on catalyst. Some of the factors influencing carbon formation in catalytic cracking have been discussed (1, 3). This catalytic coke is apparently a hydrocarbon of relatively low hydrogen content, which may vary in accordance with feed stock or operating conditions. A formula of $(C_3H_4)_n$ has been reported (4). The carbonaceous deposit also contains sulfur derived from the feed stock. However, the present discussion is concerned not with the hydrogen or sulfur content of catalytic coke but solely with the measured amount of carbon in the deposit.

Although the extent of carbon formation in catalytic cracking depends on the type of catalyst, the feed stock, and the operating conditions, it has been found that there is an intrinsic uniformity in the way the carbon deposit on the catalyst increases with time. Certain generalized correlations of striking simplicity and considerable utility have resulted from a study of such data. As this paper will show, the usefulness of the relations developed extends beyond the field of carbon yields to include an equation defining the interdependence among feed stock conversion, feed rate, and length of period between catalyst regenerations. The generalizations and derived relations apply equally to fluid and fixed-bed cracking. The results reported here were obtained in equipment ranging from laboratory size to semiplant scale. The correlations derived have been applied to the commercial-scale units.

GENERAL CONSIDERATIONS

The ordinary feed stock in catalytic cracking is a petroleum gas oil, the most volatile fractions of which have a higher boiling point than the back end of the gasoline produced. Thus, for aviation gasoline production, the initial boiling point of the feed stock will generally be above 300° F.; for motor gasoline, above

400° F. Although commercial catalytic cracking units today are employed for aviation rather than motor gasoline production, it is still convenient to refer to the feed stock conversion on the basis of production of motor gasoline. For simplicity, the products of catalytic cracking are often designated as follows:

Feed Stock	Per Cent of Feed by:
Gas (C_4 and lighter)	Weight
Total C_4	Volume
Aviation gasoline	Volume
Heavy naphtha	Volume
Cycle gas oil (400° F. initial b.p.)	Volume
Carbon (or coke)	Weight

In this system the feed stock conversion is arbitrarily taken as 100 minus volume % cycle gas oil (400° F. i.b.p.). It is realized that this expression is not an exact measure of feed stock destruction. However, it furnishes a convenient means for correlating the yields of the various products. This definition of feed stock conversion is employed in this paper.

In catalytic cracking, either fluid or fixed-bed, the extent of conversion is determined by such factors as catalyst, feed stock, temperature, pressure, feed rate, and length of time between catalyst regenerations (here called "catalyst residence time"). In fixed-bed cracking the conversion measured is the summation of the instantaneous conversions throughout the process period, the instantaneous conversions decreasing with time on stream as the catalyst becomes fouled with coke. Fluid catalytic cracking differs from fixed-bed as follows:

1. Catalyst is currently regenerated in a separate vessel, so that feed stock and freshly regenerated catalyst are continuously brought together in the reactor.
2. As a result of the above, a uniform conversion is maintained, rather than a continuously decreasing conversion as in the process cycle of fixed-bed cracking.
3. The catalyst residence time in fluid cracking is generally much shorter than the length of time between regenerations in fixed-bed work.

In either fluid or fixed-bed cracking, conversion increases with increasing temperature, decreasing feed rate, and decreasing catalyst residence time. The effect of increasing pressure, at least up to about 50 pounds per square inch gage, is to increase conversion. However, pressure was not a variable in the data presented here because substantially atmospheric pressure was employed.

In fluid cracking the feed rate is generally expressed as weight of feed per hour per weight of catalyst held in the reactor or w/hr./w. Another term employed in fluid cracking is the cata-