

# The Origin and Types of Pores in Some Alumina Catalysts

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By converting detailed nitrogen desorption isotherm data to pore-volume distributions, as many as three different pore systems have been distinguished in a single calcined catalyst. Dehydration pores are observed to be formed by the loss of water from larger crystals of alumina hydrates, either alumina trihydrates or alumina monohydrate (boehmite). These pores are small and sensitive to sintering conditions. Interparticle pores are found which appear to be developed from the packing of the ultimate particles. The volume and sizes of the interparticle pores are shown in some cases to be directly dependent on the size of the ultimate particles. When the particles are small (about 35 Å) the interparticle pore size is sensitive to the method of drying of the alumina hydrate. The size and volume of pores formed by larger particles (greater than 100 Å) can be affected by extrusion and tableting techniques.

## I. INTRODUCTION

The properties of hydrated aluminas have been admirably summarized in the monograph by Newsome *et al.* (1). Five types of hydrated alumina are of importance in catalyst preparation work prior to dehydration: the three trihydrates ( $\alpha$ -trihydrate or gibbsite,  $\beta$ -trihydrate or bayerite, and nordstrandite), a monohydrate ( $\alpha$ -monohydrate or boehmite), and amorphous alumina. These are converted to one of the various modifications of  $\gamma$ -alumina upon heating at elevated temperatures to remove moisture.

de Boer and Lippens described their technique for measuring adsorption isotherms (2) and for calculating pore-size distribution from the isotherms (2), their conclusions about the shapes of pores in aluminas from the adsorption isotherms (3), and the pore-size distributions (4). These workers showed how pores develop as alumina trihydrate and well-crystallized boehmite are calcined to remove water from a layer lattice. They also observed that the pores of microcrystalline boehmite are formed by the space between the very small irregular particles.

By converting detailed nitrogen desorption isotherm data to pore-volume distri-

butions, we have been able to distinguish as many as three different pore systems in alumina and alumina catalysts. Dehydration pores are observed to be formed by the loss of water from larger crystals of the alumina hydrates. In some cases two interparticle pore systems are found when alumina is composed of two forms differing widely in particle size. Approximate pore volumes can be assigned to each type in a consistent fashion and the size distribution of each can be defined.

Information of this type is useful in at least two ways. First of all, it helps to describe the morphology of the alumina catalyst or support, and may give information about the history of the material. Secondly, pore distribution data are used to calculate effective diffusion coefficients, a first step in estimating the possible effects of diffusional limitations in a given catalyst system (5, 6).

## II. EXPERIMENTAL

The adsorption-desorption isotherms were measured using conventional volumetric equipment, as has been described (7). The desorption isotherms were used to calculate pore-volume distributions by a method similar to that of Barrett, Joyner, and

Halenda (8). However, two changes were made in their method, made possible by use of an IBM computer for the calculations: (1) values of  $C^+$  are variable with  $P/P_0$ , and (2) for the thickness of the adsorbed film as a function of  $P/P_0$  ( $t$ ), we have used an averaged isotherm of  $V_a/V_m$  vs.  $P/P_0$  obtained from a number of nonporous materials; the data were fitted to a plot of the form  $P/P_0 = \exp [-(V/V_m)r]$  (9).

Good reproducibility is obtained with  $P/P_0 = 0.90$ , corresponding to a radius of about 1000 Å, and fair accuracy to  $P/P_0 = 0.995$ , or 2000 Å. This reproducibility is evidenced by the fact that plots of  $\Delta V/\Delta \log r$  ( $V$ , pore volume; and  $r$ , cylindrical pore radius) are reasonably smooth curves. When only one type of pore is present, as with alumina or silica-alumina gel, these distributions fit quite well to a log-normal (Gaussian) distribution. When more than one type of pore is present, as will be shown, the minimum in the distribution plot between two peaks can be used to locate the pore size which can be considered the "boundary" between the two types. By means of this "boundary" size, volumes may be assigned to each of the pore types; these results appear to be quite consistent.

It is recognized that pores will seldom, if ever, be cylindrical in shape. For most pores, in fact, the radii of curvature will be of opposite sign to cylindrical pores, if they are the voids between ultimate particles. de Boer (3) has shown, in addition, that the pores resulting from dehydration of alumina trihydrate can be slit-shaped, which one might expect from consideration of the sources of these pores. Yet, it is quite useful, and certainly simple, to consider pores as if they were indeed cylindrical, in the absence of a more general treatment. This assumption, though false, does not lead to erroneous results except for the quantitative aspects of the actual sizes, or distances between surfaces. For example, pore distribution data measured by physical adsorption merge quite well with mercury porosimetry data, in the size ranges where the two types of measurements overlap (10). Furthermore, surface areas calculated from pore distributions (PD) discussed

here agree quite well with BET areas calculated from this part of the isotherm which is usually at lower relative pressures than the part used for calculating pore distributions. Of 23 runs in this work the average ratio of PD/BET area is 0.98, with a standard deviation of 0.08 from the average. Finally, in spite of the faults in applying capillary condensation theory to very small pores, the results appear to be consistent with other knowledge.

**Alumina preparations.** The alumina trihydrates and the alumina trihydrate-boehmite-amorphous mixtures (Alumina I through V) were prepared by the addition of ammonium hydroxide solution to aluminum chloride solution (11). Sufficient ammonium hydroxide was added to bring the pH to about 8. The precipitate was filtered out and then washed by a slurry-filter method with pH adjustment to 8.0 before each filtration. Washing was continued until the chloride content of the alumina was less than 0.25% ignited weight basis. The alumina hydrate cake was then aged at ambient temperature to obtain the growth of the trihydrate phase to the appropriate level. More than 3 months are usually required to age to 100% trihydrates. Alumina I was aged 12 months.

Three general methods were used to produce the crystalline boehmite samples. Crystallite sizes of 45 to 100 Å were obtained by simultaneous addition of  $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$  solution and  $\text{AlCl}_3$  solution to boiling water (12). The temperature was held above 65°C during the addition and the slurry was refluxed to 120 hr after addition was complete. The boehmite was then washed by a slurry-filter method to less than 0.10% chloride.

Crystallite sizes of 100 to 150 Å were prepared by addition of  $\text{NH}_4\text{OH}-(\text{NH}_4)_2\text{CO}_3$  solution to a boiling  $\text{AlCl}_3$  solution (13). The resultant slurry was refluxed 120 hr and then washed by a slurry-filter method to less than 0.20% chloride.

Boehmite with crystallite sizes in excess of 150 Å were obtained by refluxing solutions containing  $\text{AlCl}_3$  and urea (14). Refluxing was continued for 120 hr after which the boehmite which had formed was washed

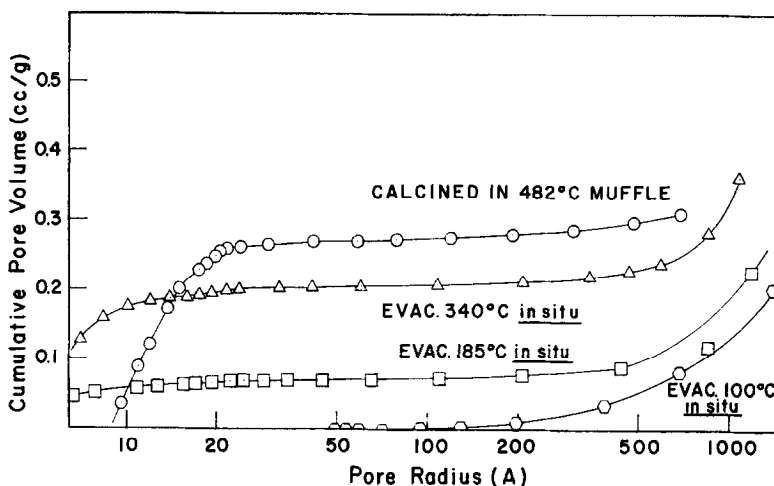


FIG. 1. Pore distributions of Alumina I.

by a slurry-filter method to less than 0.40% chloride.

**Catalyst preparation.** Catalysts were formed from oven-dry alumina hydrates by extrusion or tableting. For extrusion the alumina hydrate was milled with sufficient water in a Simpson Intensive Mixer to make an extrudable dough. The dough was extruded through a die plate with 1/16-inch diameter openings using a Welding Engineers 2-inch diameter twin-worm extruder. The extrudate was dried in an oven and broken to length.

Tableted catalyst was prepared from ground oven-dried alumina hydrate (less than 20 mesh) blended with 2% powdered vegetable stearine. The mix was tableted 1/8-inch diameter  $\times$  1/16-inch length using a Stokes RB-2 16 station tablet press.

Formed catalysts were calcined in flowing dry air at 482°C.

Analyses of the alumina hydrates for type of hydrate were carried out by our X-ray diffraction procedure (15). A Norelco Diffractometer, with Cu  $K\alpha$  radiation, was used for this purpose. By measuring the area under a suitable diffraction peak, and comparing with the corresponding area for a known sample, the percentage of a given hydrate type can be measured. The peaks of angles ( $2\theta$ ) of 18.3°, 18.5°, and 18.8° for gibbsite, nordstrandite, and bayerite constitute an envelope for total trihydrate analysis, the line at 14.5° was used for boehmite. The boehmite crystallite

sizes were calculated from the half-widths of the 38.40 line, using the Debye-Scherrer equation.

### III. RESULTS

#### A. From Pure Trihydrate Powder

Alumina I contains only trihydrates with no boehmite. The absence or near absence of amorphous alumina can be inferred from the absence of extraneous pore systems, and the low surface area of 11 m<sup>2</sup>/g of Al<sub>2</sub>O<sub>3</sub>. Figure 1 shows essentially no small pores, when this alumina trihydrate is evacuated at 100°C, below the decomposition temperature. The pores which appear at a size greater than 200 Å must be due to interparticle spaces between these 0.5 to 2  $\mu$  particles.

Upon evacuation in situ at 185°C, with a 10.2% loss in weight, pore volume and surface area (162 m<sup>2</sup>/g) are created, but apparently of a pore size too small to be measured. Evacuation in situ at 340°C, to 32.1% loss, leads to the production of more pore volume and surface area (467 m<sup>2</sup>/g), again to pores too small to be measured by this technique. In either case, the calculated average pore radius or slit size ( $2V/S$ ) is 9 Å. This type of observation is interesting because of the consistency of the data with other observations, in spite of the fact that the Kelvin equation should not apply to such size.

When the same alumina is calcined in a muffle furnace at 900°F to a LOI of 4.4%, still more pore volume is apparently created, and the surface area becomes 480  $\text{m}^2/\text{g}$ ; however, the pores are in the 9–20 Å region. We believe this enlargement is due to a self-steaming. It is possible, and even probable, that the lower pore volume observed after evacuation at 340°C in reality represents only those pores accessible to nitrogen, and that some void

volume may be present which is inaccessible, but becomes so on steaming.

### B. Trihydrate-Gel Mixtures

Alumina II consists of 14% boehmite and 86% alumina trihydrate. All three alumina trihydrate phases were identified in the sample.

Figure 2 shows that even uncalcined this alumina powder has appreciable porosity. The distribution plot, Fig. 2B, has

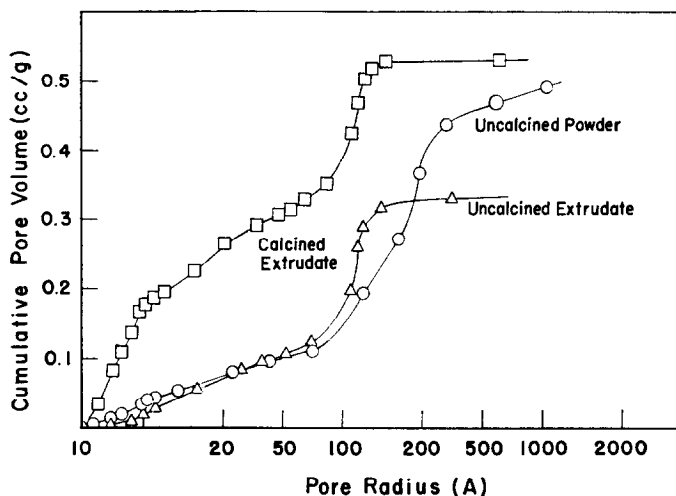


FIG. 2A

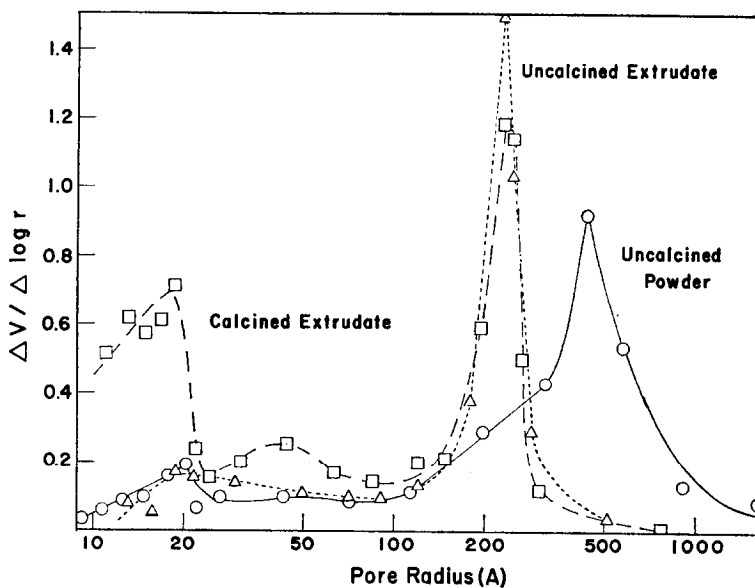


FIG. 2B

FIGS. 2A, B. Effect of forming and calcination on Alumina II.

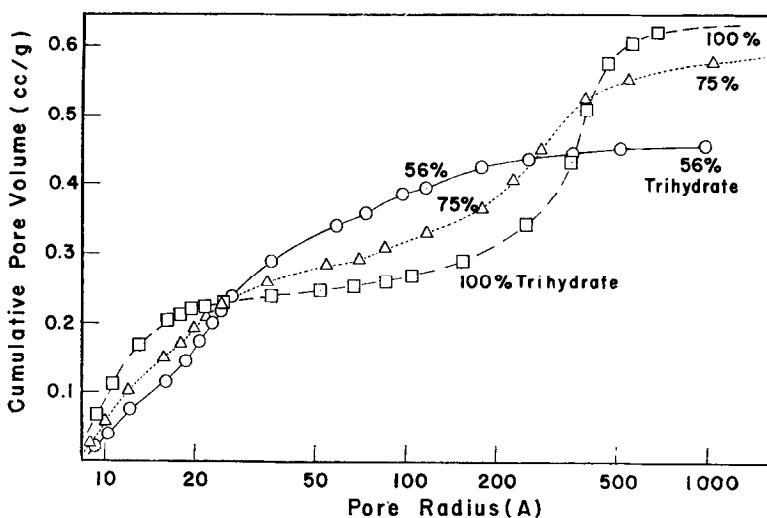


FIG. 3A

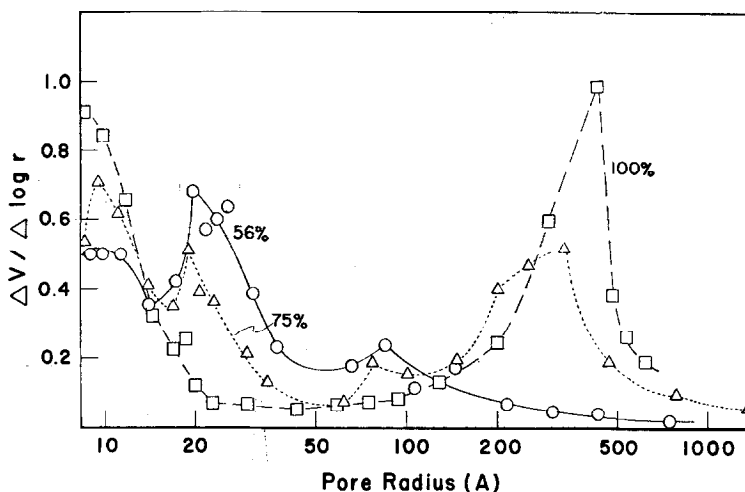


FIG. 3B

FIGS. 3A, B. Effect of trihydrate content of alumina precursor on calcined tablets of Alumina III.

two peaks. The broad macropore peak at about 400 Å may be designated as volume between the relatively large trihydrate particles. The peak at about 20 Å is also an interparticle volume, related to the small size of the ultimate boehmite particles. Upon forming this powder into pills, by extrusion, essentially only the macropores are affected, although the small pores are somewhat compressed.

Upon calcination, a significant change takes place, in that dehydration pores are produced. The conditions of calcination

in this particular case were such that the peak is close to 20 Å.

The distinction between pores of different types is made more clear by examining a series in which the alumina trihydrate content was varied. Alumina III was prepared by precipitation and subsequent aging to various trihydrate levels. At each level, a portion was tableted,  $1/8 \times 1/16$  inch, and calcined at 482°C in a stream of air. Some of the resulting pore distributions are shown in Fig. 3.

The gradual development of more small

TABLE 1  
ALUMINA III

Percent trihydrate	Surface area (m <sup>2</sup> /g)	Pore volume assignments			Total <sup>a</sup>
		Dehydration	Boehmite	Macro	
56	427	0.102	0.211	0.151	0.464
62	437	0.144	0.186	0.201	0.531
70	446	0.140	0.158	0.297	0.595
75	457	0.159	0.128	0.322	0.609
85	481	0.185	0.072	0.438	0.695
93	481	0.205	0.075	0.409	0.689
100	502	0.210	0.039	0.389	0.638

<sup>a</sup> Nitrogen data agree with pore volumes by He-Hg displacement.

pores as percent trihydrate increases is apparent from the figures. In the distribution plots of  $\Delta V/\Delta \log r$  vs.  $r$ , which are approximations to the derivatives of the cumulative pore volume plots, maxima are noted at about 10 Å, at about 19 Å, and at 150-400 Å. Thus, there are three types of pores present in these materials: (1) the dehydration pores, arising from the trihydrate; (2) small interparticle pores, initially present, and altered only by moisture loss during calcination; and (3) the macropores. As stated above, the latter are the voids between the trihydrate particles.

We have chosen to utilize the radii at the minima in the distribution plots as the boundary between the types of pores; by reference to the cumulative plots, one can assign volumes to each type of pore. Table 1 lists these values for the samples of Alumina III.

The increase in volume assigned to dehydration pores with an increase in trihydrate content is apparent. These two parameters are plotted in Fig. 4, which includes similar data for several other extruded aluminas, to show the generality of the correlation. As would be expected, the boehmite pore volume decreases as trihydrate content increases. However, a plot similar to Fig. 4, but with boehmite pore volumes replacing dehydration pore volumes, does not show the general correlation when different preparations of alumina are included. This boehmite phase appears to be sensitive to the conditions of precipitation and drying.

The macropore volume, and total pore volume, reach a maximum at about 85% trihydrate in this series. This is in some respects an accident, since macropore volume is the result of tableting compression. In another sense, it is not an accident, since an attempt was made to keep tableting conditions as uniform as possible.

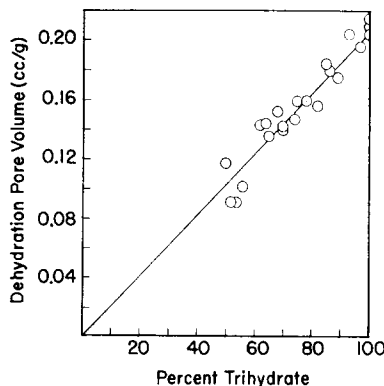


Fig. 4. Dehydration pore volume of calcined catalyst vs. trihydrate content of alumina precursors.

The fact that a dehydration pore volume of 0.20 cc/g is observed at 100% trihydrates rather than the 0.26 cc/g for Fig. 1, is curious. Probably, in those aluminas in which 100% trihydrates are reported, the real value is somewhat less, as attested by an observation of some boehmite pore volume (Table 1). By contrast, the alumina of Fig. 1 had no boehmite pore volume.

The dehydration and boehmite pore sintering can be followed separately. Figure 5 shows how, by increasing the severity of calcination of Alumina IV (82% tri-

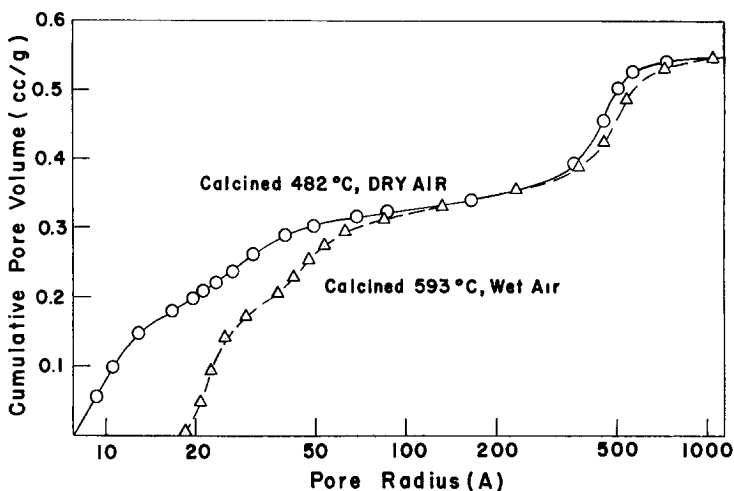


FIG. 5A

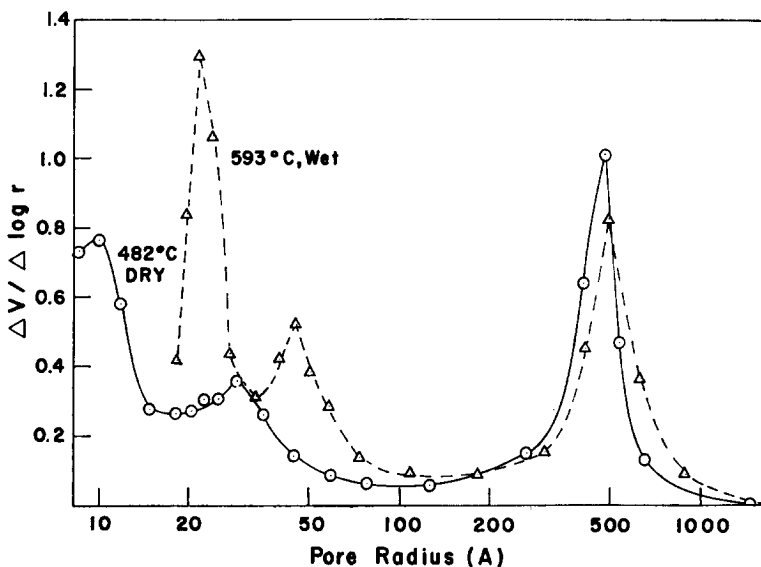


FIG. 5B

FIGS. 5A, B. Effect of calcination conditions on Alumina IV.

hydrates) resulting in lower surface area, each type of pore is separately enlarged. The macropores, on the other hand, are not affected by the sintering, as is to be expected.

The boehmite pores are gel-like, if we may use as a criterion their tendency to be affected by their mode of drying. Kistler (16) showed some years ago that a gel would not shrink when dried above the critical temperature of the medium to

produce an aerogel; the "normal" pore sizes are observed when dried from aqueous media, whose surface tension causes collapse from the highly dispersed hydrogel to the more compact xerogel.

We have conducted similar experiments with a series from Alumina V, allowed to age to three different trihydrate levels. At each level, one portion was oven-dried; the water in the remainder was exchanged for methanol, which has a lower surface

tension than water, and subsequently dried. This constitutes what is termed a "semi-aerogel" (17) technique: larger gel pores should be observed, but not the dehydration pores.

In Fig. 6 we see that methanol exchange had no effect either on the dried 100% trihydrate alumina, or on the material subsequently calcined at 482°C to produce dehydration pores. As expected, these pores have no gel-like characteristics.

On the other hand, the boehmite alumina is indeed gel-like, as demonstrated in Fig. 7, for Alumina V-B material of the 73% trihydrate level, and Fig. 8 for V-C at 52%.

Clearly, therefore, methanol exchange has no effect on the 100% trihydrate structure, which has no pore volume to start with; nor does it affect the structure of the dehydration pores of the subsequently calcined material. There is an effect at the 73% trihydrate level which becomes more pronounced at 52%; in either case, the pore volume is increased, while at the same time the distribution shifts to larger pore sizes. Thus, that alumina which is not trihydrate alumina has the characteristics of alumina gel.

### C. Boehmite Aluminas

When an alumina is prepared, for example, by precipitation with ammonia from a solution of an aluminum salt, and subsequently

XRD Cryst. Size (Å)	Boehmite surface area (m <sup>2</sup> /g)	Calcined catalyst surface area (m <sup>2</sup> /g)	Catalyst dehydration pore volume (cc/g)
49	345	339	0
57	—	305	0
62	285	299	0
81	272	272	0
85	268	268	0
91	225	284	0
94	227	261	0
105	234	287	0.03
112	171	255	0.015
113	154	283	0.03
127	159	264	0.04
129	120	256	0.09
137	153	264	0.05
145	72	278	0.09
169	54	227	0.06
175	57	229	0.07
182	23	262	0.10
182	57	249	0.09
188	—	223	0.07

dried, it has the characteristics of a gel. In this context is meant the existence of porosity and of appreciable surface area. As we have seen, the conditions of drying affect the morphology of the alumina.

Other factors involved in the pore distribution of aluminas are the size and shape of the ultimate particles. We have developed

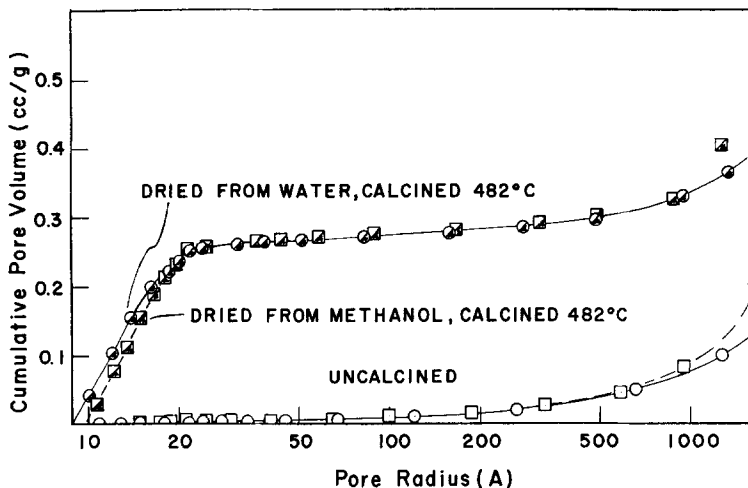


FIG. 6. Effect of methanol exchange on Alumina V-A (100% trihydrates).



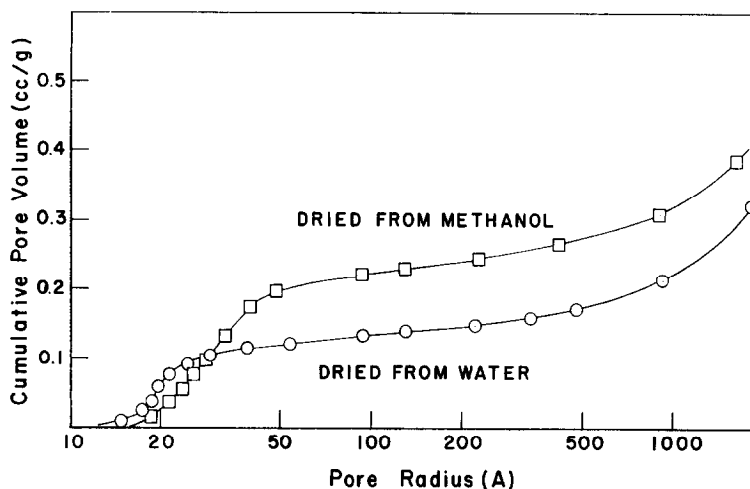


FIG. 7A

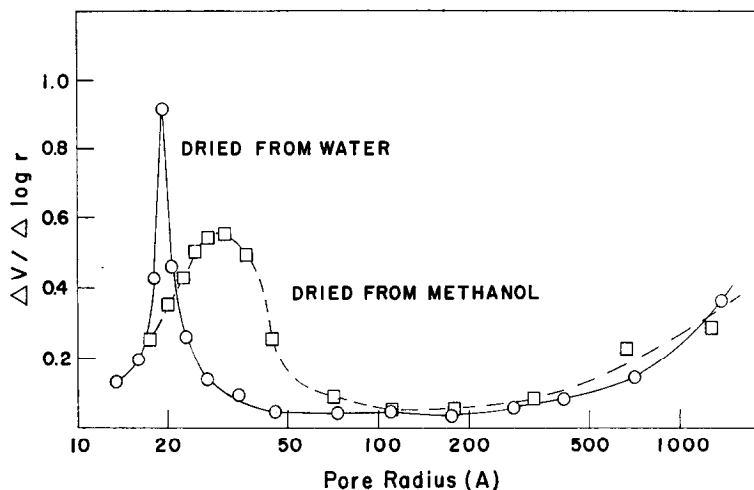


FIG. 7B

Figs. 7A, B. Alumina V-B (73% trihydrates).

techniques for preparing boehmite in various crystal sizes. No attempt was made to define a shape factor, but the sizes, in relative terms, were obtained from the X-ray diffraction half-widths. A number of boehmites, with crystallite sizes so determined which vary from 49 to 188 Å, have been examined. The pore distributions of four of these are depicted in Fig. 9. A number of these boehmites have been extruded into catalyst supports and calcined. In Fig. 10 is a plot showing total pore volume of the finished catalyst as a function of the XRD crystallite size of the

original boehmite. Figure 11 is a plot of the major pore size of the catalysts vs. boehmite crystallite size. While we recognize that the half-width of an XRD peak is the result of defects in the crystalline structure as well as of crystallite size, the measurement is useful for the relative value of size. The X-ray measurement is ambiguous in any case because different values are obtained from different peaks in the pattern. We have been arbitrary in our selection of the 38° peaks.

Another measure of size may be obtained from surface area. In Table 2 are given the

X-ray crystallite sizes and surface areas of a series of boehmites. Also in the table are the surface areas and dehydration pore volumes of extruded and tableted catalysts prepared from these boehmites. The surface areas of the boehmites without very serious exception show the trend of lower surface

area with larger crystallite size. It is impossible to make a calculation of size from surface area, but the crystallite sizes of the materials of less than  $150 \text{ m}^2/\text{g}$  appear to be far too small to be particle sizes. These crystallite sizes may be reflecting defects in the boehmite structure rather

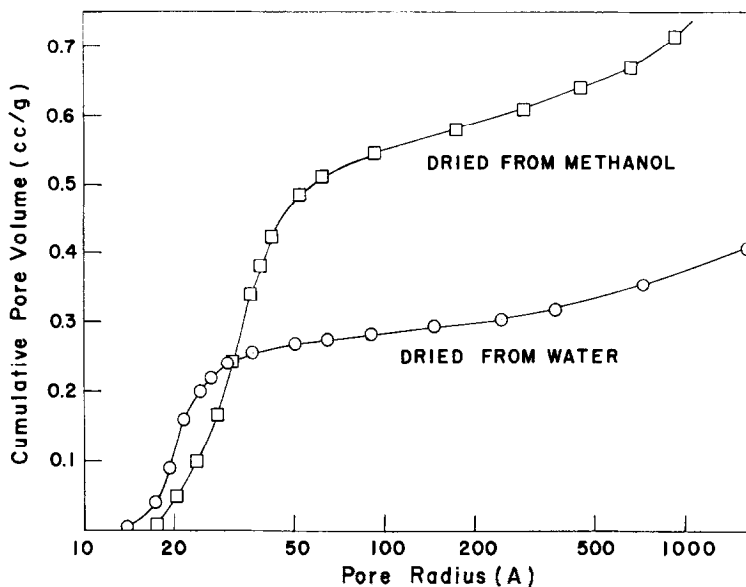


FIG. 8A

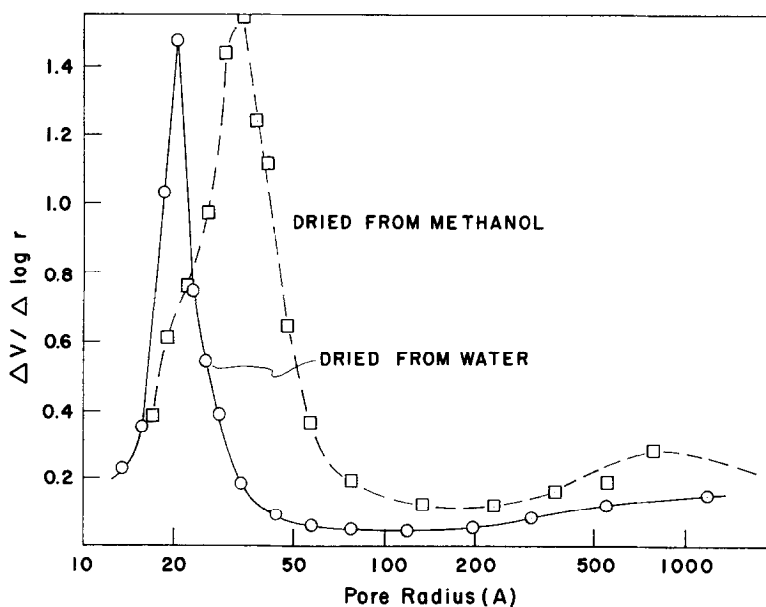


FIG. 8B

Figs. 8A, B. Alumina V-C (52% trihydrates).

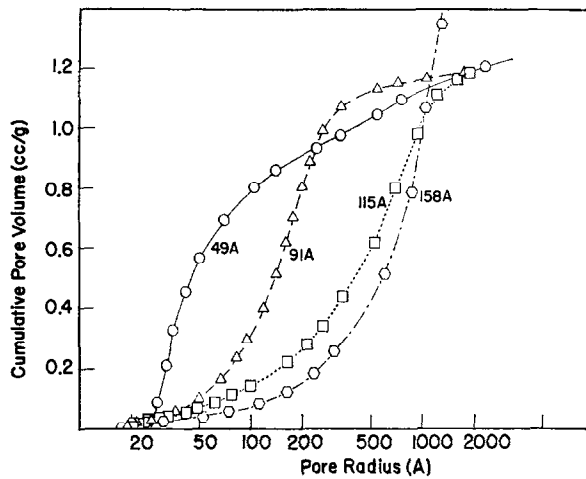


FIG. 9A

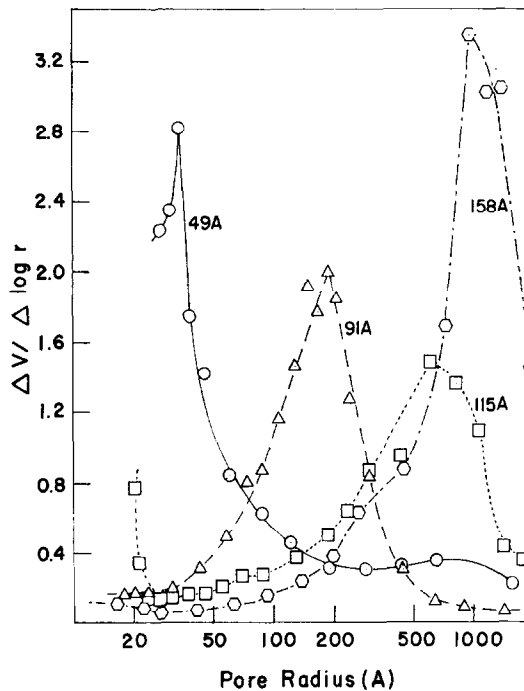


FIG. 9B

FIGS. 9A, B. Boehmite aluminas having various crystallite sizes.

than the ultimate particle sizes which may be two/five times the XRD values. Surface areas of the calcined catalysts are relatively constant compared to the more than tenfold change in the surface areas of their boehmite precursors. This indicates an increase in area in the dehydration pores as we go down the series that fairly well compensates for the decrease in surface on the exterior of the boehmite crystals.

#### IV. DISCUSSION

We can distinguish between the various pore systems in alumina catalysts and relate their properties to the characteristics of the precursor alumina hydrates. In general there are two types of pore, those which appear because of dehydration of the alumina hydrates and those which are the voids between the alumina hydrate particles.

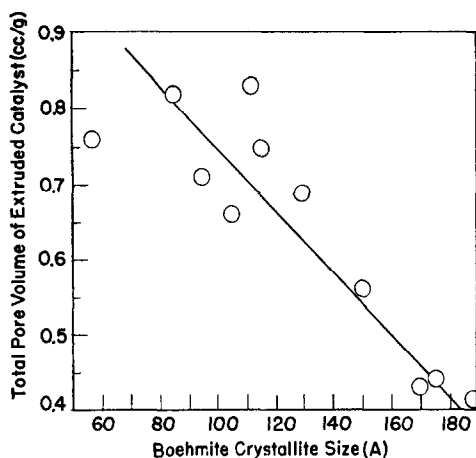


FIG. 10. Effect of boehmite crystallite size on pore volume of catalyst.

The alumina hydrates are layer structures, and removal of water during dehydration causes the layers to become thinner. Dehydration pores form between the layers as water is removed. If this could be accomplished without disturbing the remainder of the lattice the pores which formed would be too small to admit nitrogen. We have never observed this, but when extreme caution has been taken in dehydration, pores have been so small that equilibration with nitrogen was slow. The pores that develop are so small that the size cannot be measured by our techniques. Careful dehydration of the alumina trihydrates of Fig. 1 has produced pores of less than 10 Å. Generally the dehydration is not carried out this carefully and the

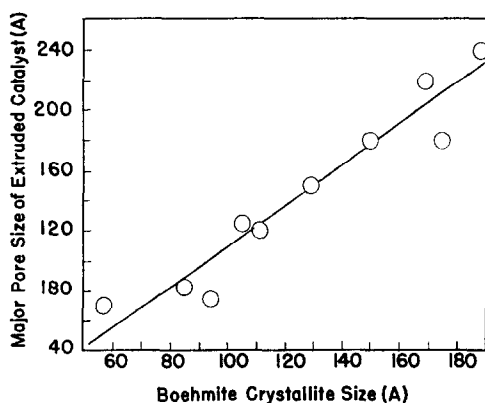


FIG. 11. Effect of boehmite crystallite size on pore size of catalyst.

pores are enlarged by self-steaming, such as the muffle-furnace-calcined alumina of Fig. 1. Further enlargement will occur under more severe conditions of sintering, such as by increased temperature or water partial pressure.

The maximum dehydration pore volume can be calculated from the densities of the solid phases if we assume no particle shrinkage. Our helium displacement measurements of the density of  $\gamma\text{-Al}_2\text{O}_3$  average 3.48 g/cc. Using 2.42 g/cc for gibbsite (1) and 3.01 g/cc for boehmite (1), we calculate a maximum dehydration pore volume of 0.34 cc/g from the trihydrate, and 0.10 cc/g from boehmite. We have nearly reached the maximum for dehydration of boehmite. The maximum we have achieved for dehydration of trihydrates is 0.26 cc/g, as shown in Fig. 1, for example. The difference between 0.26 and 0.34 can be accounted for by a linear shrinkage of 4%.

de Boer and Lippens have observed the formation of narrow pores and increased surface area by calcining well-crystallized boehmite at 450° to 580°C. Their microcrystalline boehmites do not behave in this fashion. This is consistent with the data in Table 2 which show no dehydration pore volume for catalysts prepared from boehmite having crystallite sizes below 100 Å. When crystallite sizes are appreciably above 100 Å and surface areas of the boehmites are low, the maximum theoretical value is attained.

The boehmite precipitated at room temperature usually gives a crystallite size by XRD of about 35 Å. When this material is dried the pore system develops with pores about 20–35 Å. These are clearly the spaces between the particles. Pores of this size are usually not affected by the means we use to form catalysts, that is, tableting and extrusion. Rather, they respond to the techniques which are used for maintaining porosity of gels through the drying step. Specifically replacement of water by methanol has allowed us to dry this type of material with increased pore volume as shown in Figs. 7 and 8.

At the other extreme large crystals, such as we obtain by aging the boehmite to form trihydrates, also give a pore struc-

ture with pores of size comparable to the crystal size. In this case, however, the pore volume and size are sensitive to the forming techniques, but are not sensitive to the drying procedure.

The series of boehmites we have worked with are of intermediate sizes. When these were tableted little relationship of pore size or pore volume to crystallite size was found. However, catalysts formed by extrusion give us a relationship of both pore volume and pore size to crystallite size. This comes about as a result of conditions of extrusion. The free moisture required to make an extrudable dough from these materials is a function of the surface area, therefore crystallite size, of the boehmite. High surface area materials require more moisture and subsequently dry to a higher pore volume. Mulling the boehmite with water to make the extrudable dough lubricates the particles so that under compression in the extruder they compact with voids of sizes dependent on the size of the ultimate particles.

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