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Studies on Pore Systems in Catalysts III.
Pore-Size Distribution Curves in Aluminum Oxide Systems

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The pore-size distributions of the pore systems described in the previous publication are quantitatively examined. The conclusions are in harmony with those derived from the shape studies. There is a definite difference in sintering behavior between boehmite-based preparations and bayerite-based aluminas. The cumulative specific surface areas are compared with those obtained by the BET method.

1. INTRODUCTION

The method of calculation of pore-size distributions for slit-shaped pores and the correction values for the thickness t of the multimolecularly adsorbed nitrogen layer, described in article I of this series (*1*), have been applied to the isotherms of the various alumina preparations, described in article II (*2*).

Starting from high values of the relative pressure, we continued the calculation down to a relative pressure of 0.08. Mathematically this would correspond to a Kelvin radius, $r_k = 3.7$ Å, and consequently with slit-shaped pores to a width of $d = r_k + 2t = 10.7$ Å. Though it is scarcely possible to connect the physical significance of the conception of capillary condensation with the part of the isotherms below a relative pressure of about 0.3 ($r_k \sim 8$ Å; $d = r_k + 2t \sim 18$ Å), we nevertheless may draw some significant qualitative conclusions from it.

2. THE DISTRIBUTION CURVES

Figures 1, 2, 3, and 4 show the cumulative surface areas $S_{\mathrm{cum}(x)}$, of the pore systems contained in all pores with a width larger than d_x. As stated above x varies from $x = 1$ to $x = 0.08$.

Gelatinous boehmite (A 120) has a very broad pore-size distribution, ranging from about 100 Å down to 16 Å, as could be expected from electron microscope observations. As already stated in article II of this series (*2*) this is also in accordance with the conclusion drawn from the shape and the sloping character of the hysteresis loop. The calculation of the pore-size distribution has to be continued beyond the relative pressure at which the hysteresis loop closes [at x $(p/p_0) = 0.40$]. This points to capillary condensation in pores with shapes not leading to hysteresis phenomena, as may be expected from wedge-shaped or conical pores at the contact points of the fibrillar particles.

On heating, the narrowest pores disappear, and the wider pores are widened somewhat. Only the curves of A 450 and of A 750 are shown in Fig. 1. With A 750 the calculation ends at the point where the hysteresis loop starts; the wedge-shaped pores seem to have disappeared by rounding off the contact points. The same conclusion was drawn in article II from the disappearance of the type E character of the hysteresis loop.

As stated in article II of this series MiBoV shows a pronounced E type hysteresis loop. Accordingly also here the pore-size distribution calculation has to be continued beyond the closing point of the hysteresis loop; wedge-shaped pores of small size, not giving

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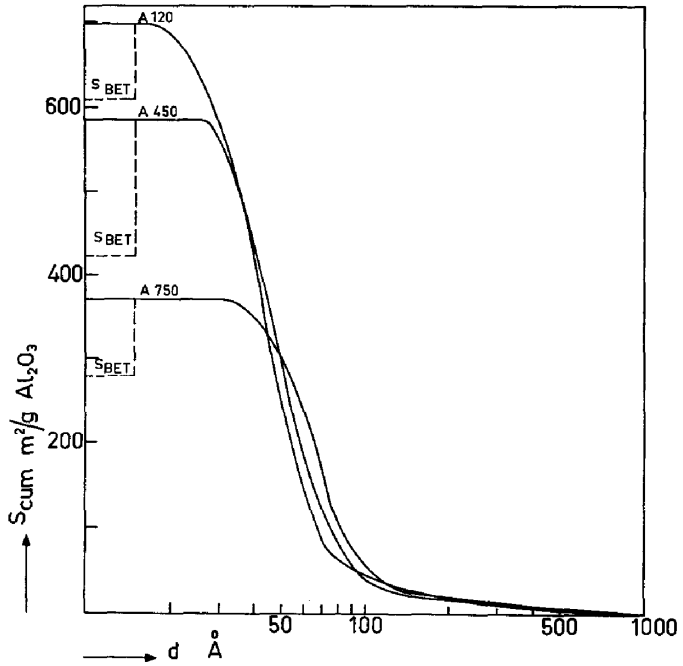

Fig. 1. Cumulative surface areas, S_{cum}, of gelatinous boehmite and of two of its dehydration products.

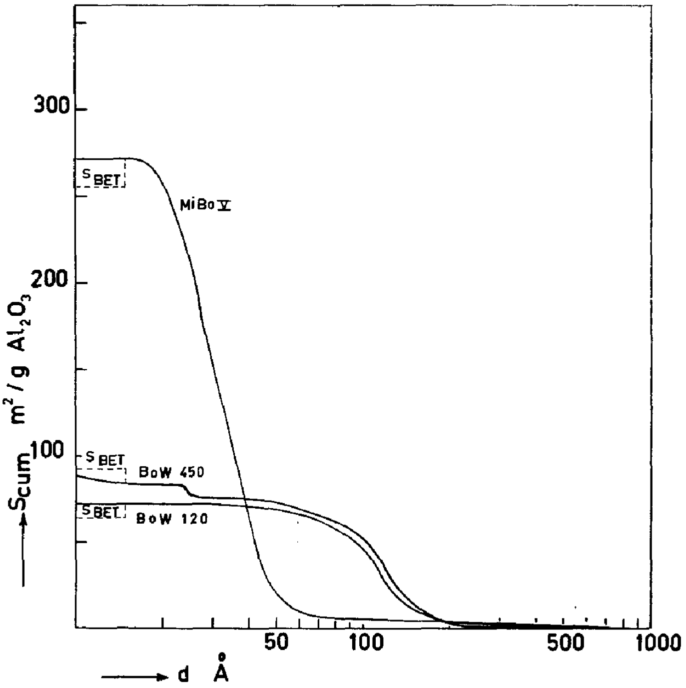

Fig. 2. Cumulative surface areas, S_{cum}, of microcrystalline boehmites and one of the dehydration products.

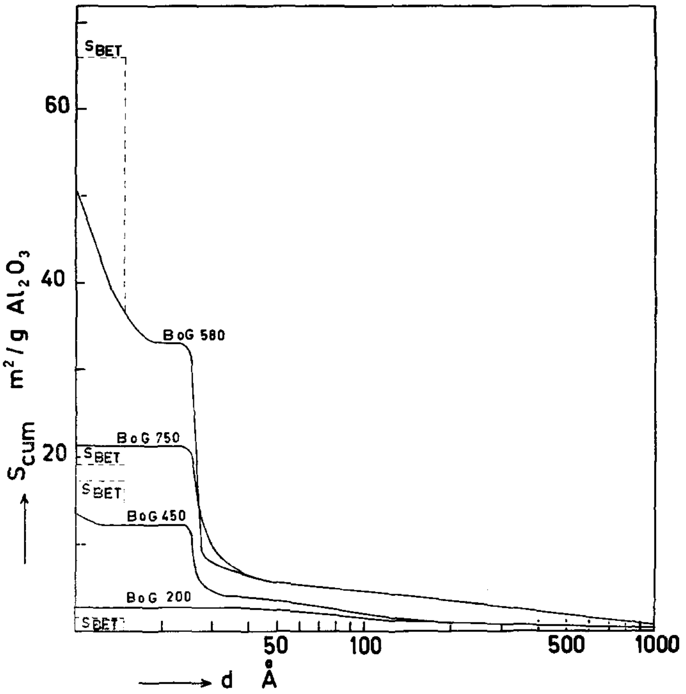

FIG. 3. Cumulative surface areas, S_{cum}, of some dehydration products of well-crystallized boehmite.

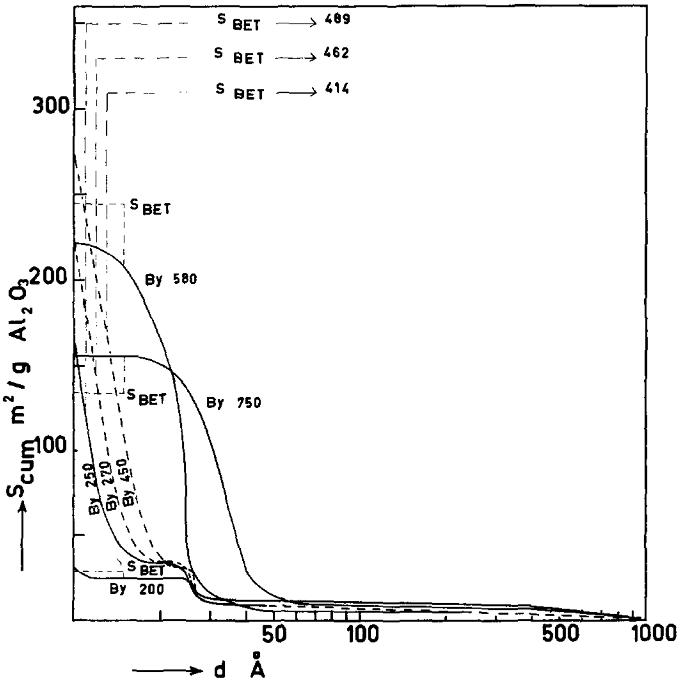

FIG. 4. Cumulative surface areas, S_{cum}, of bayerite and one of its dehydration products.

rise to hysteresis phenomena, are present between the small irregularly shaped particles.

Sample BoW 120, which has lost the E type hysteresis loop for an A type loop (see article II), when it was prepared from gelatinous boehmite by hydrothermal treatment, accordingly does not show narrow pores beyond the closing point of the hysteresis loop. Sample BoW 450, however, shows some narrower pores, which may have formed by decomposition of the boehmite at 450°C. The adsorption isotherm of BoW 450 in article II shows an extension of the hysteresis loop, accordingly.

The pore-size distribution curves of well-crystallized boehmite and its thermal decomposition products (BoG samples) are completely in accordance with the results obtained from the analyses of the hysteresis phenomena in article II of this series. It is remarkably clear that the narrow pores, formed by heating at 450°C and, especially, at 580°C, disappear by sintering phenomena, which occur during heating at 750°C, as suggested in article II.

The aluminas made from the crystalline hydroxides give a quite different picture. The hysteresis loops of the samples By 200, 250, 270, and 450, demonstrate the occurrence of pores with a width of about 25 Å. It is remarkable, moreover, to note the increasing amount of very narrow pores, already slightly present at By 200, but far more pronounced in the samples By 250, 270, and 450. The sintering at higher temperatures, leading to the disappearing of the very narrow pores, is clearly demonstrated by the curves for By 580 and By 750. In both cases, however, the distribution curve still shows the presence of pores, narrower than those corresponding with the closing end of the hysteresis loop. This, again, is in accordance with the pronounced E type character of the hysteresis loops, as discussed in article II.

3. Comparison of Some Data of the Distribution Curves with Experimental Data from Other Measurements

Table 1 shows the values of the cumulative pore volumes and surface areas, contained in pores with widths down to $d = \sim 18$ Å (columns 4 and 5, respectively) and to $d = \sim 11$ Å (columns 6 and 7, respectively). These figures may be compared with those measured directly. V_p (column 2), the pore volume of the various samples was taken from the experimental isotherm. Theoretically it may be derived from the total amount of liquid nitrogen, taken up by adsorption and by capillary condensation just below the saturation pressure of liquid nitrogen. The adsorption isotherms, however, are very steep in this region of relative pressures and for practical reasons we took the point on the desorption branch of the nitrogen adsorption isotherm at a relative pressure of $x = 0.999$. This pressure corresponds to a Kelvin radius, $r_k = \sim 1\,\mu$ (10^4 Å); a large part of the intergranular space is, therefore, included in this figure. S_{BET} is the specific surface area, determined by the normal BET technique.

Columns 8 and 9 give the ratios between the cumulative properties at a relative pressure $x = 0.3$ and the figures which are measured more directly.

In a number of cases the ratio $S_{\mathrm{cum}\ 0.3}/S_{\mathrm{BET}}$ is greater than 1, whereas $V_{\mathrm{cum}\ 0.3}$ is almost equal to V_p.

de Boer (*3*) mentioned a number of reasons why S_{cum} may be greater than S_{BET}. Pores may intersect, the volume of the intersections is not bounded by the surface of the solid, but it is included when calculating S_{cum}. In the case of pores with widened parts (type E or some type A hysteresis loops) the volume of these parts is attributed to pores that are narrower. In these cases it may be expected that S_{cum} lies between once and twice S_{BET}. Large pores with narrow openings (some type B hysteresis loops) also give too high values for S_{cum}, in this case even up to many times S_{BET}.

For our samples it appears that in nearly all cases in which the ratio $S_{\mathrm{cum}\ 0.3}/S_{\mathrm{BET}}$ is greater than 1, the hysteresis loop is of type A or E. Only sample BoG 750 belongs to type B. Moreover, in all these cases the cumulative quantities calculated down to a relative pressure of 0.3 are almost equal to those calculated down to 0.08. Pores nar-

TABLE 1
CUMULATIVE PORE VOLUMES AND SURFACE AREAS

Sample	V_p	S_{BET}	$V_{\mathrm{cum}\ 0,3}$	$S_{\mathrm{cum}\ 0,3}$	$V_{\mathrm{cum}\ 0,08}$	$S_{\mathrm{cum}\ 0,08}$	$V_{\mathrm{cum}\ 0,3}/V_p$	$S_{\mathrm{cum}\ 0,3}/S_{\mathrm{BET}}$
Gelatinous boehmite								
A 120	1.982	609	1.954	697	1.954	697	0.99	1.15
A 450	2.042	414	2.158	586	2.158	586	1.06	1.42
A 750	1.547	280	1.651	372	1.651	372	1.07	1.33
Microcrystalline boehmite								
MiBo V	0.520	255	0.524	268	0.527	271	1.01	1.05
BoW 120	0.435	64	0.443	72	0.443	72	1.02	1.13
BoW 450	0.494	92	0.498	83	0.501	87	1.01	0.90
Well-crystallized boehmite								
BoG 200	0.034	1.5	0.034	2.7	—	—	—	—
BoG 450	0.056	17.1	0.055	12.1	0.055	12.8	0.98	0.71
BoG 580	0.222	65.7	0.186	33.1	0.196	47.1	0.84	0.50
BoG 750	0.139	19.1	0.140	21.2	0.140	21.3	1.01	1.11
Bayerite								
By 120	0.068	5.0	0.068	2.5	—	—	—	—
By 200	0.454	26.5	0.458	25.6	0.459	27.2	1.01	0.97
By 250	0.500	489	0.313	34.2	0.374	129	0.63	0.07
By 270	0.495	462	0.311	38.8	0.410	194	0.63	0.08
By 450	0.495	414	0.330	57.2	0.459	245	0.67	0.14
By 580	0.534	245	0.500	187	0.527	221	0.94	0.76
By 750	0.526	134	0.539	155	0.540	156	1.03	1.16

rower than 15 Å therefore do not occur. For the other samples $S_{\mathrm{cum}\ 0.3}$ is smaller than S_{BET}, sometimes even very much smaller. Even $S_{\mathrm{cum}\ 0.08}$ is often smaller than S_{BET}. The same holds for the volumes. These samples apparently contain a number of narrow pores, the size distribution of which may certainly not be calculated on the basis of the Kelvin equation.

This latter kind of pores appears to originate mainly during the dehydration of the crystalline compounds. Qualitatively it can be stated that these pores grow wider as the heating temperature is higher; at a sufficiently high temperature (750°C) they have disappeared entirely (with the samples originating from boehmites), or nearly completely (bayerite).

Steggerda (*4*), when investigating the aluminas obtained by heating gibbsite, tried to calculate the mean width of the narrow pores (d_s) in his samples with the equation:

$$d_s = 2 \cdot \frac{V_p - V_{\mathrm{cum}\ 0.3}}{S_{\mathrm{BET}} - S_{\mathrm{cum}\ 0.3}}$$

Using this equation we obtain for our samples with both $(S_{\mathrm{cum}\ 0.3}/S_{\mathrm{BET}}) < 1$ and $(V_{\mathrm{cum}\ 0.3}/V_p) < 1$ the following results:

Sample	BoG 450	BoG 580	By 250	By 270	By 450	By 580
d_s(Å)	4.0	22	8.2	8.7	9.3	11.7

Though this method is more real than one assuming a liquid meniscus in pores with a width smaller than twice the diameter of the adsorbate molecules, it includes all the systematic difference between the cumulative quantities and their real values. Only in those cases that $S_{\mathrm{cum}\ 0.3}$ is very small compared with S_{BET} can somewhat more reliable results be expected (By samples).

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