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Studies on Pore Systems in Catalysts II. The Shapes of Pores in Aluminum Oxide Systems

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Complete adsorption–desorption curves of nitrogen have been measured on aluminum oxide systems, including boehmites of various origin and bayerite, as well as aluminas obtained by dehydrating these starting materials by heating at various temperatures. The hysteresis loops can be described according to a classification given in an earlier study; they belong to types A, B, or E, or combinations of them, of that classification. The conclusions with respect to the shapes of the pores which can be drawn from these curves are discussed. The pores of gelatinous boehmite and of the aluminas obtained from it consist of the spaces between the small fibrillar particles which form sheets. At higher temperatures the pores widen and the pore walls smoothen.

Microcrystalline boehmite prepared by hydrothermal conversion of sheetlike gelatinous boehmite at 150°C, is built up from very small irregularly shaped particles and its pores are formed by the spaces between these particles. Hydrothermal treatment at higher temperatures yields far more regularly shaped platelets, forming pores with approximately rectangular cross sections.

Well-crystallized boehmite shows a different pore system; on heating very narrow pores are formed in addition to the wide original ones, but they disappear again by heating at higher temperatures.

Bayerite preparations behave more or less as gibbsite, described in an earlier publication.

1. Introduction

The various forms of aluminum hydroxide and of aluminum oxyhydroxide, as well as the manifold types of aluminum oxide obtained from them by dehydration, have been studied during the last ten or more years by the Delft research group and by many other investigators.

In the present and following publications a more systematic analysis is attempted with respect to sizes, shapes, and distribution of various types of pores in them and with respect to the genetic relations between the pores of various preparations. The measurements were performed with the apparatus described in the first paper of this series (*1*).

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The present article will deal mainly with the conclusions which may be drawn from the shapes of the isotherms and hysteresis loops with respect to the shapes of the pores, making use of a classification which was published a few years ago (*2*).

2. Starting Materials

The aluminum hydroxides used were:

A, gelatinous boehmite obtained from ammonium alum and sodium aluminate;

MiBo, microcrystalline boehmite obtained by heating gelatinous boehmite A in liquid water at 150°C in an autoclave;

BoW, microcrystalline boehmite obtained by heating gelatinous boehmite A in liquid water at 250°C in an autoclave;

BoG, well-crystallized boehmite obtained by heating a commercial gibbsite (containing

12.5 mg Na_2O/g of Al_2O_3) in liquid water at 250°C in an autoclave;

By, bayerite made by Schmäh's method (*3*) from amalgamated aluminum metal (99.99% Al) by reacting with water of pH 7 at room temperature.

All hydroxides were dried at 120°C in air and analyzed for sulfate, sodium, and iron, while the loss of water on heating was determined by heating to 1200°C (Table 1)·

TABLE 1
COMPOSITION OF HYDROXIDES[a]

Sample	H_2O	SO_3	Na_2O	Fe
A	309	1.2	0.15	0.21
BoW	197	0.2	0.10	0.05
BoG	195	0.1	0.10	0.03
By	546	[b]	[b]	0.02

[a] All quantities expressed in mg per gram Al_2O_3.
[b] Not detectable.

The aluminas were obtained by heating the hydroxides in air at the desired temperature till constant weight; they are distinguished in the text by adding a suffix denoting the heating temperature. A further description and details of preparation are given in the doctor's thesis of B. C. Lippens (*4*).

3. THE ADSORPTION–DESORPTION ISOTHERMS OF NITROGEN AT LIQUID NITROGEN TEMPERATURE

Figures 1, 2, 3, and 4 give the isotherms of a number of our samples. All show a reversible part at low pressures and a hysteresis loop at higher pressures. The shapes of the reversible parts as well as those of

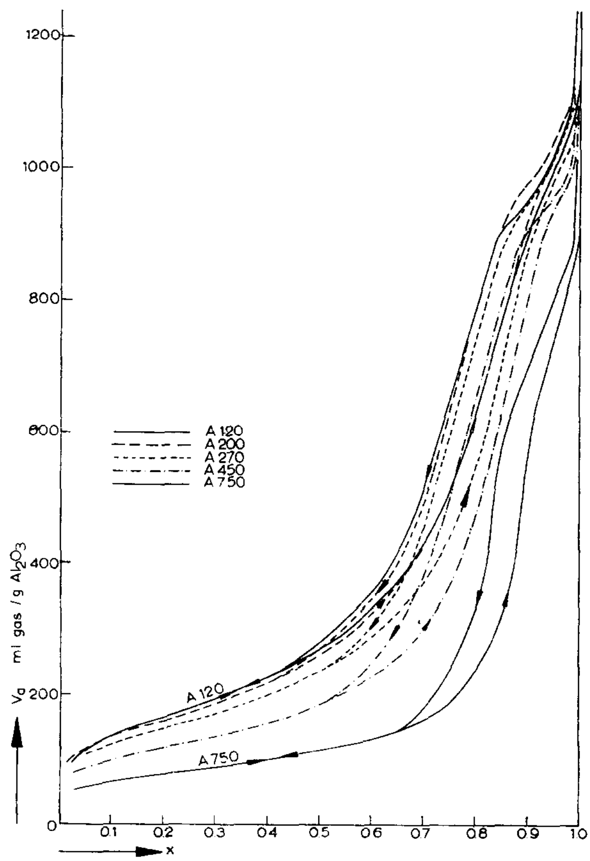

FIG. 1. Nitrogen adsorption isotherms of A preparations.

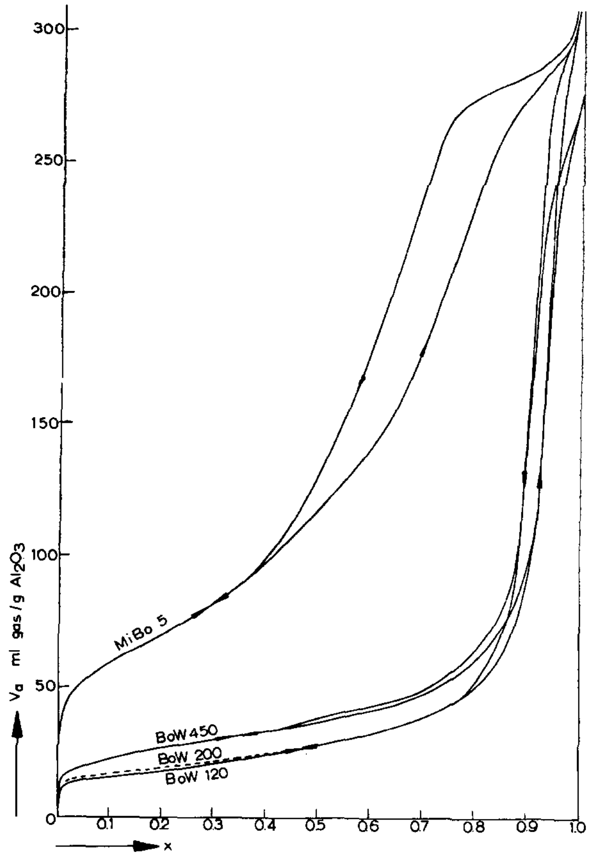

FIG. 2. Nitrogen adsorption isotherms of microcrystalline boehmites and products obtained by heating them.

the hysteresis loops differ greatly from sample to sample. The hysteresis loops correspond to types A, B, and E (or combinations of them) (Fig. 5) of a classification given in an earlier study (*2*).

Type A with two very steep branches can be related to tubular pores, with various forms of cross section, open at both ends with no or only slightly widened parts, or to "ink bottle" types of pores, with wide or with very short necks.

Type B is a hysteresis loop with a vertical adsorption branch at a relative pressure very close to one and a desorption branch at some medium pressure. Such a hysteresis loop can be formed by very wide pores having narrow short openings or by pores formed by parallel plates at some distance from each other (slit-shaped pores).

Type E, with a steep desorption branch and a sloping adsorption branch has much resemblance to type A. This type can be attributed to tubular pores with openings of some effective radius r_n and with widened parts with varying radii $r_w > 2r_n$. If there is a variation in the radius r_n for the different pores the desorption branch too will have a sloping character, but the broadening of the loop upwards still exists.

4. CONCLUSIONS WHICH MAY BE DRAWN FROM THE ISOTHERMS

The isotherms of sample A (gelatinous boehmite) and the aluminas obtained from it all have a hysteresis loop of type A combined with a little of type E in the higher relative pressure region, hence with the wider pores. The higher the heating tem-

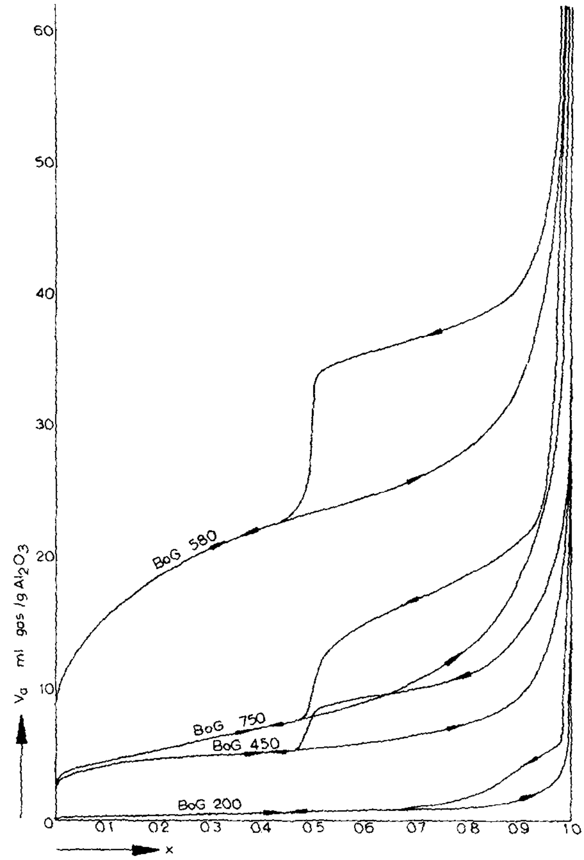

FIG. 3. Nitrogen adsorption isotherms of heated preparations of well-crystallized boehmite.

perature the less pronounced the type E character. In the type A parts of the hysteresis loops

$$(p_a/p_0)^2 < p_d/p_0$$

This relation may point to cross sections of the tubular pores, which may be described by a rectangular cross section (*2*), with a short side a and a longer side na. At higher relative pressures, where the difference in thickness of the adsorbed layer, t, between those of the adsorption branch and of the desorption branch is small with respect to the pore width, such cross sections lead to:

$$(p_a/p_0)^{(n+1)/n} = p_d/p_0$$

n having a value between 2 and 3 in the present case.

The shape and the sloping character of the hysteresis loop is in accordance with the electron microscope picture of gelatinous boehmite as given by Souza Santos *et al.* (*5*) and by Moscou and van der Vlies (*6*): In sheets formed by small fibrillar particles a broad pore spectrum (sloping branches of the hysteresis loops) is to be expected, as well as the presence of tubular, though short, pores with widened parts. The disappearance of the type E character for samples heated at a higher temperature can partly be ascribed to the smoothing of the pore walls by sintering (contact places of the fibrils) and also to the general widening of the pores on heating (*7*), increasing the widths of the narrower parts of the pores to those of the wider parts.

The changes occurring during hydrothermal conversion of sheetlike gelatinous boehmite into microcrystalline gelatinous boehmite (*4*) can be followed by comparing

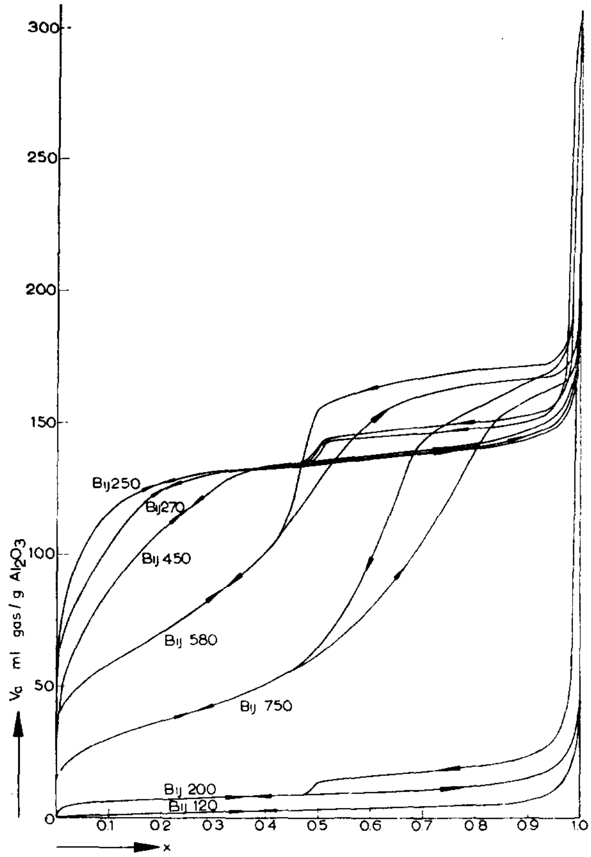

FIG. 4. Nitrogen adsorption isotherms of bayerite and some of its dehydrated products.

Figs. 1 and 2. Sample MiBo 5, which is obtained from sheetlike gelatinous boehmite A 120 by hydrothermal treatment at 150°C, gives a loop with pronounced type E character, which is in line with its being built up from very small irregularly shaped particles.

Sample BoW 120 is obtained from sheetlike gelatinous boehmite A 120 by hydrothermal treatment at 250°C. The type E character of the hysteresis loop has disappeared completely. BoW 120 consists of small, six-sided, platelets, the packing of which gives rise to the formation of pores with approximately rectangular cross section (type A loop), the two effective diameters of which can be described by one dimension being 2 to 3 times larger than the other. As shown by the curves for BoW 200 and BoW 450, the character of these pores is not altered by heating to the indicated temperatures.

The aluminas obtained by heating well-crystallized boehmite BoG give adsorption isotherms characterized by a type B loop, pointing either to very wide pores with narrow openings or to slit-shaped pores. From the very steep part at relative pressures near one it follows that there are a number of very wide pores which have to be attributed to the space between the particles. The shapes of the isotherms of BoG 450 and BoG 580 suggest that a great number of narrow pores form by heating well-crystallized boehmite to these temperatures, causing the specific surface area to increase substantially. These pores are too narrow to allow capillary condensation with hysteresis phenomena. Heating to 750°C causes sintering phenomena by which the narrow pores disappear and the specific surface area decreases again substantially.

Bayerite preparations, when heated just

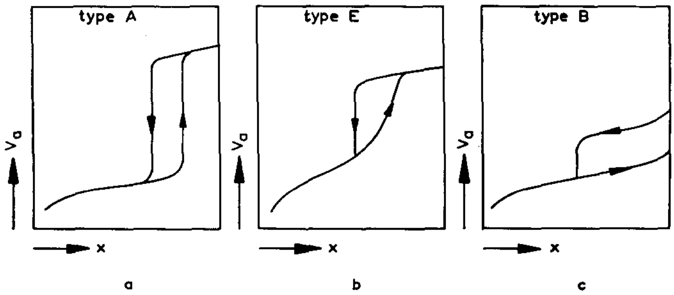

FIG. 5. Three types (A, B, and E) of the classification of hysteresis loops.

above their decomposition temperature, give isotherms with a small hysteresis loop of type B, indicating the forming of very wide pores with narrow openings or of slit-shaped ones. Heating to 250°C causes a large increase in surface area, a phenomenon comparable to that found with the other crystal modification of aluminum hydroxide, viz. gibbsite (*7*, *8*). This increase is, here, also caused by the forming of many narrow capillaries, as is indicated by the steep rise of the isotherm at low values of the relative pressure, x; these capillaries are filled by normal multimolecular adsorption and they give no hysteresis phenomena. The hysteresis loop of type B, already present with By 200 is also found with the preparations heated to 250°C, 270°C, and 450°C, just as was found with gibbsite, as, e.g., shown by curve PSH 344 (gibbsite heated to 344°C) in a previous publication (*7*, Fig. 4). Heating to temperatures above 450°C shows the influence of sintering. The narrow capillaries disappear gradually and they are converted into wider pores, showing hysteresis of type E character.

Subtracting the hysteresis loop of By 200 from curve By 580 yields a pure type E hysteresis curve and so does the same procedure with curve By 750. In the latter case the sloping character has increased noticeably, indicating that in the course of further sintering a greater variety in effective diameters r_n is caused. As shown by the isotherm, the specific surface area decreases immensely during this process. The whole sequence of phenomena resembles that found earlier with gibbsite (*7*), where also curve PSH 580 (*7*, Fig. 7) is a combination of the B type hysteresis loop of preparations heated to lower temperatures and an E type curve.

A quantitative analysis of the pore-size distribution of the preparations described above appears in the following paper of this series.

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