

Studies on Pore Systems in Catalysts IV. The Two Causes of Reversible Hysteresis

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The nitrogen sorption isotherms of gibbsite, heated at 205°C and at 245°C, have been measured. Heating at 205°C, causing intragranular hydrothermal decomposition, yields pores of the ink-bottle type, while heating at 245°C results in slit-shaped pores. An analysis of the nitrogen isotherms to distinguish between the two types of pores is given.

1. THE CAUSES OF REVERSIBLE HYSTERESIS PHENOMENA

Reversible hysteresis phenomena in the capillary condensation part of adsorption-desorption curves of gases (vapors) in pores of catalysts may be caused by two different mechanisms. In 1931 Kraemer (1) suggested reversible hysteresis to be caused by pores with wide bodies, closed on all sides but for a narrow neck opening. This "ink-bottle" theory was worked out in more detail by McBain (2). In 1932 another possibility was forwarded by Foster (3), who suggested that reversible hysteresis might be due to the existence of pores, open on all sides. In the adsorption branch (rising pressures) no meniscus of capillary-condensed liquid exists, as it can only be formed when the adsorbed film grows thick enough to block the pore somewhere. At the desorption branch the meniscus is present and governs the relative pressure in the pore.

As, obviously, open capillaries are far more useful for purposes of catalysis than ink-bottle types, methods of analysis, distinguishing between the two types are wanted. In some cases the shape of the hysteresis loop may give a clue.

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Ink-bottle pores with narrow and short necks, in which the multimolecular layer (of N₂, e.g., at liquid nitrogen temperatures), together with capillary condensation along the edges forms an "effective" cylindrical radius r_n , while the rather wide bodies show an "effective" cylindrical radius r_w such that

$$r_w > 2r_n$$

show wide hysteresis loops with adsorption and desorption branches at the intermediate relative pressures, p_a/p_0 and p_d/p_0 , respectively, obeying the relation (4):

$$(p_a/p_0)^2 > p_d/p_0 \quad (1)$$

Cases, obeying this relation seem to be fairly rare.

There are, however, many cases, obeying:

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

These narrow hysteresis loops of type A (4) may either be caused by wide-necked ink-bottle type pores, where

$$r_n < r_w < 2r_n$$

or by tubular capillaries, open at both ends, but possessing slightly widened parts (or one narrowed part), where the same relation holds, or by open tubes with rec-

tangular cross sections ("effective" oval-shaped meniscus along the walls at the adsorption branch).

Similarly a hysteresis branch at, or nearly at saturated pressure and a desorption branch at intermediate relative pressures may be due either to ink-bottle type pores with very wide bodies and narrow short necks

$$r_w \gg 2r_n$$

or to open slit-shaped capillaries with parallel walls.

2. THE CAPILLARY SYSTEM IN DEHYDRATION PRODUCTS OF GIBBSITE

When aluminum trihydroxide, $\text{Al}(\text{OH})_3$, is dehydrated by heating, various stages of developing the pore system have been observed. In gibbsite (the same holds for bayerite) an intergranular hydrothermal conversion (δ) is observed at temperatures between about 160° and about 200°C . The development of water starts at the active spots in the gibbsite granules and on the surface. The water inside the granules cannot escape quickly enough and builds up a relatively high water-vapor pressure, converting gibbsite into boehmite and water which escapes only slowly by diffusion. By further elevating the temperature the water forces its way out, thus creating some pores connected with the outside and releasing the internal pressure. Inside the granules the conversion into boehmite has left some holes, which are now connected with the outside by pores, just created. At 205°C the development of these narrow necked "ink-bottles" is complete.

From optical investigations it appears that the normal decomposition, starting now, proceeds in two stages. In the temperature range of about 225 – 250°C the first stage takes place; the water molecules originate from OH groups in the (001) planes of the hexagonal gibbsite crystals, producing slit-shaped pores. At 245°C the specific surface area (BET) is about 50 times as large as at 205°C . So it is allowed to suppose that the holes of the original "ink-bottles," which are, anyway, now also

connected with the outside by many capillaries, will not seriously contribute to the total surface.

The dehydration product at 245°C is negatively birefringent in contrast with the original gibbsite, which is positively birefringent. The negative birefringence of the partially decomposed product is due to a form-birefringence—the optical axis is perpendicular to the original cleavage plane of gibbsite. This behavior points to slit-shaped pores.

If the heating is continued above 250°C the plates are divided into rodlike particles by proceeding dehydration. For the purposes of the present examination we did not proceed into this third stage, but we chose the two samples, mentioned above, viz. the ink-bottle pores, made up till 205°C and gibbsite heated to 245°C , which shows a set of parallel slit-shaped open pores.

The nitrogen isotherms of these samples, measured in a micro-BET apparatus (described in part I of this series, ref. 6) are given in Fig. 1.

3. THE EQUILIBRIUM PARTS OF THE HYSTERESIS LOOPS

If ink-bottle type pores are responsible for the hysteresis, the adsorption part represents the equilibrium part of the sorption curves (?). At the desorption branch the capillary-condensed liquid in the "bottles" is retained at relative pressures far below their equilibrium values, as given by the Kelvin equation

$$\ln p/p_0 = -2\sigma V \cos \gamma / RT r_k$$

where σ is the surface tension of the sorbate, V its molecular volume, γ the contact angle between the sorbate and the solid 0° in our case, and r_k is the so-called Kelvin radius. In the body of the holes, r_k has a rather high value, but the liquid is not released until the relative pressure has been lowered to a value corresponding with the r_k value of the narrow neck.

With the slit-shaped pores, however, we have a completely different situation. At the desorption the filled pores have a

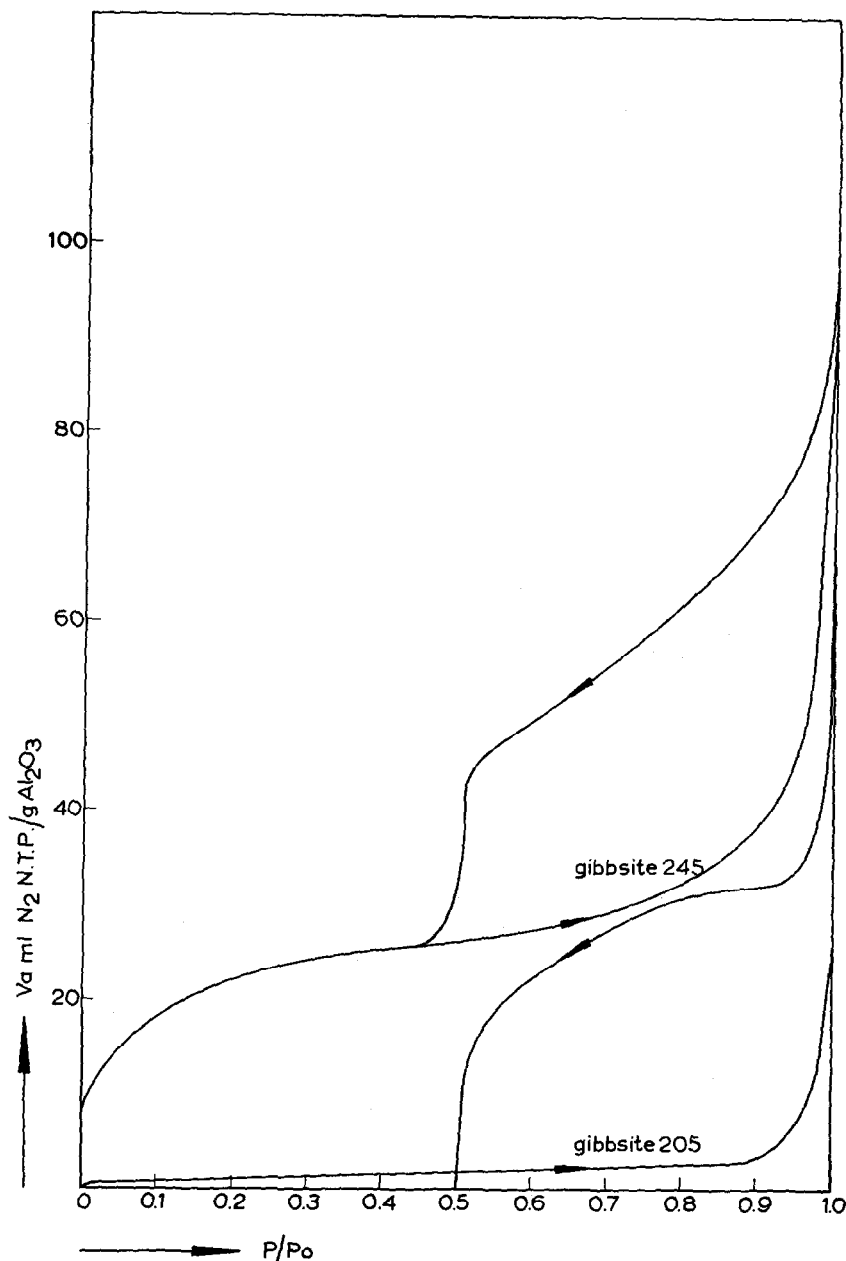


Fig. 1. Nitrogen adsorption isotherms of heated gibbsite.

meniscus, the Kelvin radius of which can easily be related with the real pore width of the capillaries, viz. $r_k = d - 2t$, where d represents the pore width and t the thickness (δ) of the adsorbed (multimolecular) layer which is independent of the capillary condensation. At any point of the

desorption branch the liquid in all pores is in equilibrium with both the capillary condensation and adsorption phenomena. During the adsorption to meniscus can be formed; the pores will only be filled with adsorbate, until the adsorbed layers on the pore walls make contact with each other.

Hence, in the case of slit-shaped pores the desorption part of the isotherm represents the equilibrium part of the sorption curves.

4. DISTINCTION BETWEEN THE TWO SHAPES OF CAPILLARIES

The difference of stable and unstable parts of the isotherms gives us a method for distinguishing between pores of the ink-bottle type and slit-shaped pores.

With the ink-bottle type an analysis, using the desorption branch as described in I of this series (8), but modified for cylindrical pores, the volume of the "bottles" of the pores is wrongly connected with the size of the "neck," which leads to a far too large cumulative surface area, hence $S_{cum}^{des} > S_{BET}$. Neglecting the volume of the "neck" with respect to the "bottle" and considering the "bottle" as a nearly closed cylinder or as a system of cylinders with different sizes, the Kelvin radii of the liquid surface in the adsorption branch correspond to the actual pore sizes. Here we do not account for small errors, caused by dividing the "bottles" in cylinders, hence $S_{cum}^{ads} = S_{BET}$.

For slit-shaped pores an analysis of the adsorption branch with the method described earlier (6) gives a shifting of the pore spectrum to wider pores. This corresponds with a too small cumulative pore surface, or $S_{cum}^{ads} < S_{BET}$. When, however, the pore-size distribution is calculated from the desorption branch of the isotherm S_{cum}^{des} must be equal to S_{BET} .

From Section 2 above, we know that the pores of gibbsite heated at 205°C (gibbsite 205) are of the ink-bottle type. So we know, that calculating the pore-size distribution from the desorption branch gives $S_{cum}^{des} > S_{BET}$. This is already indicated in previous work of this laboratory (9). Calculating the pore-size distribution from the

adsorption branch will result in $S_{cum}^{ads} = S_{BET}$.

Gibbsite heated at 245°C (gibbsite 245), however, has slit-shaped pores. Applying the calculation of the pore-size distribution—for this type of pores—must give for the desorption branch $S_{cum}^{des} = S_{BET}$ and for the adsorption branch $S_{cum}^{ads} < S_{BET}$.

The results of the calculations are given in Table 1 and Figs. 2 and 3.

From the table we see, that the results are in striking agreement with our expectations. The agreement of the cumulative pore volumes and the actual pore volumes confirm our choice for the right sorption branch in calculating the pore-size distribution (see underlined values in Table I.)

In general the agreement will be less good. In most cases the pores will have a more irregular shape or show a mixture of several shapes. For these cases S_{BET} will have a value in between S_{cum}^{ads} (assuming cylindrical pores) and S_{cum}^{des} (assuming slit-shaped pores).

We proved this by making mixed samples of the above-mentioned components gibbsite 205 and gibbsite 245. In all cases the measured specific surface area (BET) of the mixture appeared to be equal to that which is obtained by addition, in the right ratio, of the specific surface areas of the two components. This value was, however, always intermediate between S_{cum}^{ads} and S_{cum}^{des} , calculated for the mixed samples.

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TABLE 1
CUMULATIVE PORE VOLUMES AND SURFACE AREAS

Sample	H ₂ O (%)	S_{BET} (m ² /g Al ₂ O ₃)	S_{cum}^{ads} (m ² /g Al ₂ O ₃)	S_{cum}^{des} (m ² /g Al ₂ O ₃)	V_p (ml/g Al ₂ O ₃)	V_{cum}^{ads} (ml/g Al ₂ O ₃)	V_{cum}^{des} (ml/g Al ₂ O ₃)
Gibbsite 205	30.6	<u>1.6</u>	<u>2.1</u>	76	<u>0.075</u>	<u>0.073</u>	0.116
Gibbsite 245	23.0	<u>77</u>	42	<u>74</u>	<u>0.151</u>	0.138	<u>0.151</u>

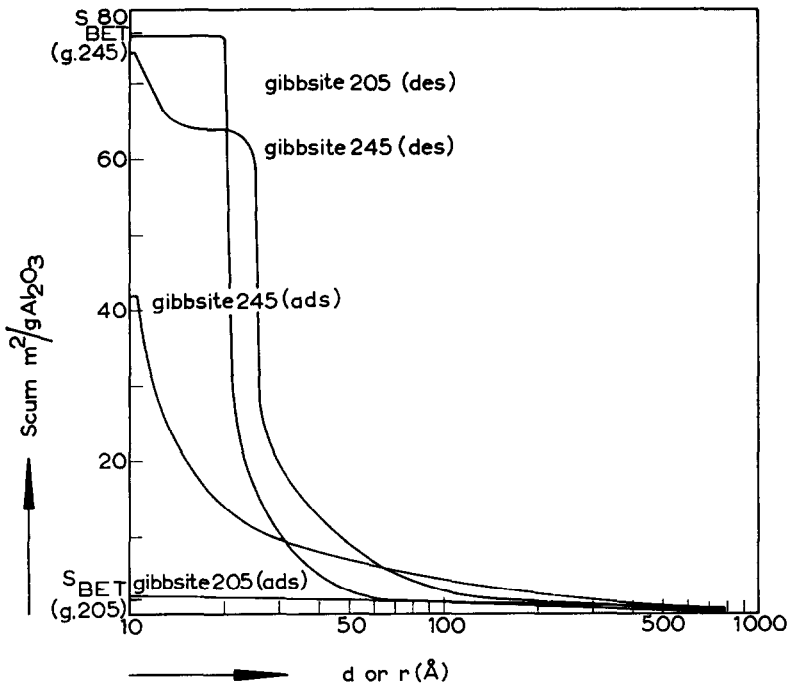


FIG. 2. Cumulative surface area S_{cum} of heated gibbsite.

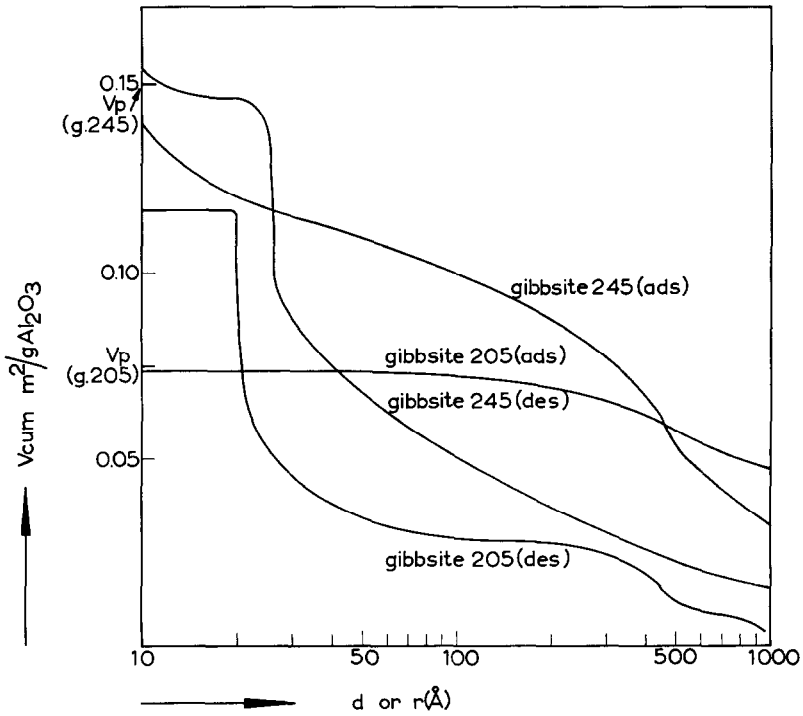


FIG. 3. Cumulative pore volume V_{cum} of heated gibbsite.

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