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Thermal Decomposition of Gibbsite Under Low Pressures

I. Formation of the Boehmitic Phase

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The incomplete transformation of gibbsite $Al(OH)_3$ into boehmite $AlO(OH)$ during the course of its thermal decomposition is explained with the help of a model involving both a diffusion of hydroxyls either along the "structural channels" of the gibbsite microcrystal or along the cleavage planes and a desorption of water. This study is based mainly on experiments carried out with micron-size samples, involving thermal analysis under controlled pressure and constant decomposition rate.

INTRODUCTION

During the past 20 years, much atten-ion has been paid to the preparation of 'active" aluminas by means of the thermal lecomposition of gibbsite $Al(OH)_3$ (also ;alled "hydrargillite" or, after Edwards ;t al. (*1*), "α-alumina trihydrate"). Among he main research contributions, we must [uote those of the Aluminum Company of merica and of the Compagnie Pechiney, ogether with those of the Dutch and of the yon schools, to which more detailed reference will be made in the following. In spite f this, there is still no complete agreement oncerning the mechanism of the thermal ecomposition of gibbsite.

The reason seems to lie in the complexity f the mechanism of this reaction, as illus-ated by the great number of schemes iven, for instance, by Trambouze (*2*) and y Dethy (*3*) to describe the crystalline odifications of what were formerly called γ-aluminas," these phase transitions hav-g first been distinguished by Stumpf al. (*4*).

It follows that much of the past work nnot be easily compared because even ight experimental differences (which are erefore easily omitted) can determine the xture or development of structure. For stance, let us only recall that an increase of 1 Torr in the water vapor pressure above a gibbsite sample during its thermal decomposition is enough to change the specific surface area accessible to nitrogen from 56 to 320 m^2g^{-1} (*5*).

Therefore, our aim is to present a contribution to the knowledge of the mechanism of thermal decomposition of gibbsite by controlling very carefully several parameters which appear to play here an important part (true vapor pressure in the close neighborhood of the gibbsite grains, decomposition rate, particle size).

With the help of differential thermal analysis (D.T.A.), the thermal decomposition of industrial gibbsite (obtained by the Bayer process) can be easily divided into three steps (*6–8*):

(a) partial dehydration of gibbsite $Al(OH)_3$ which is transformed into boehmite $AlO(OH)$ (also called "α-alumina monohydrate," after (*1*));

(b) formation of a "transition" alumina partly hydrated, itself undergoing a complex transformation during the course of further thermal treatment;

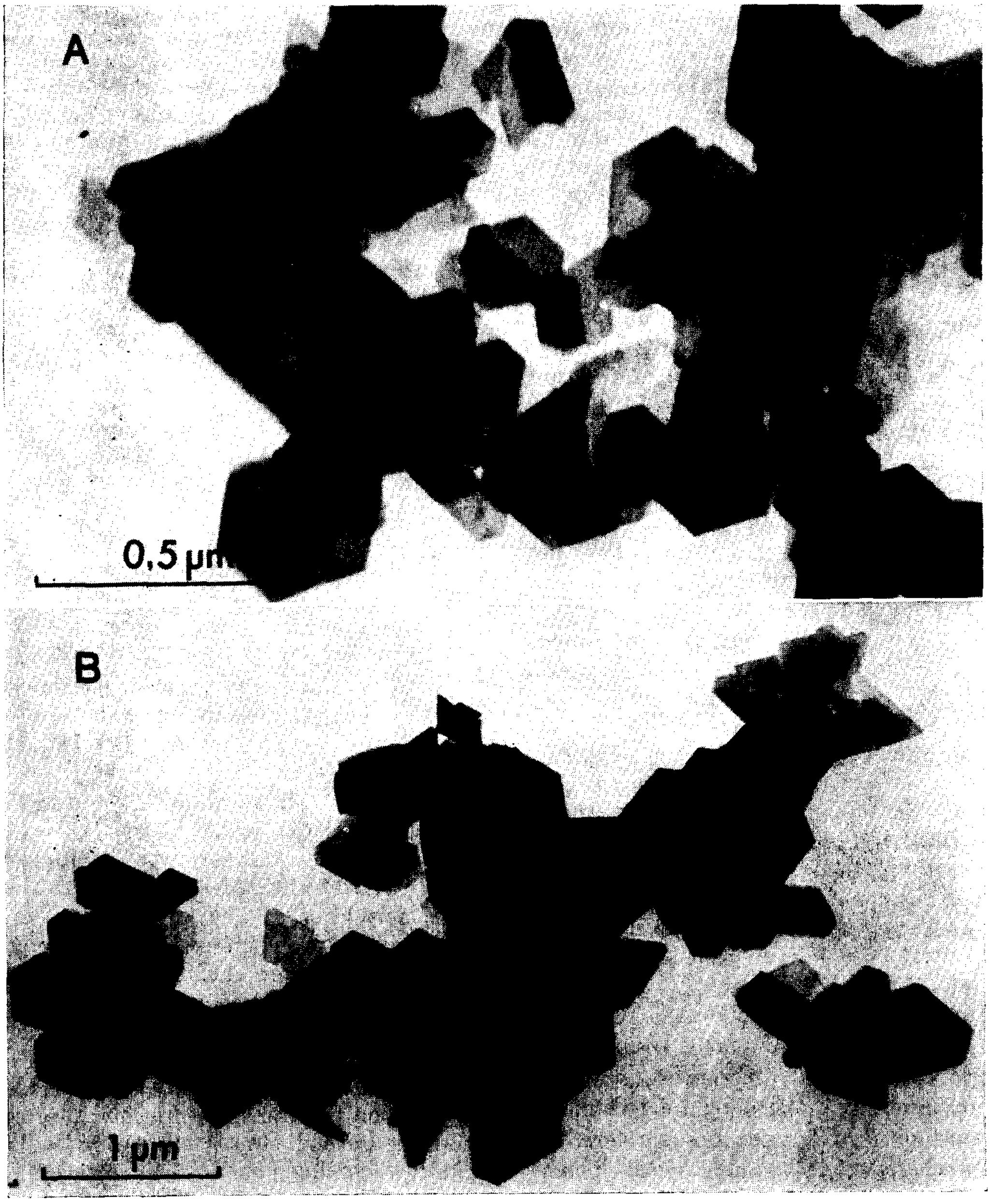
(c) thermal decomposition of the boehmite formed during the first step.

We shall focus our attention on the first step and on the transition towards the second (the second step itself being studied in a forthcoming paper). The state of affairs may be summarized as follows: No complete agreement has been achieved among the different authors about the incomplete character of the first step (*9*) and two different schemes have been suggested in order to explain the transition from the first to the second step (*7, 10*). In the present work we shall, therefore, try to advance new results in order to solve this question and, in a more general way, to set up a mechanism which could account for the influence of the parameters which are controlled here.

A. Samples and Experimental Methods

I. *Samples*

Figure 1 shows a micrograph of each of the three gibbsite samples under investiga-



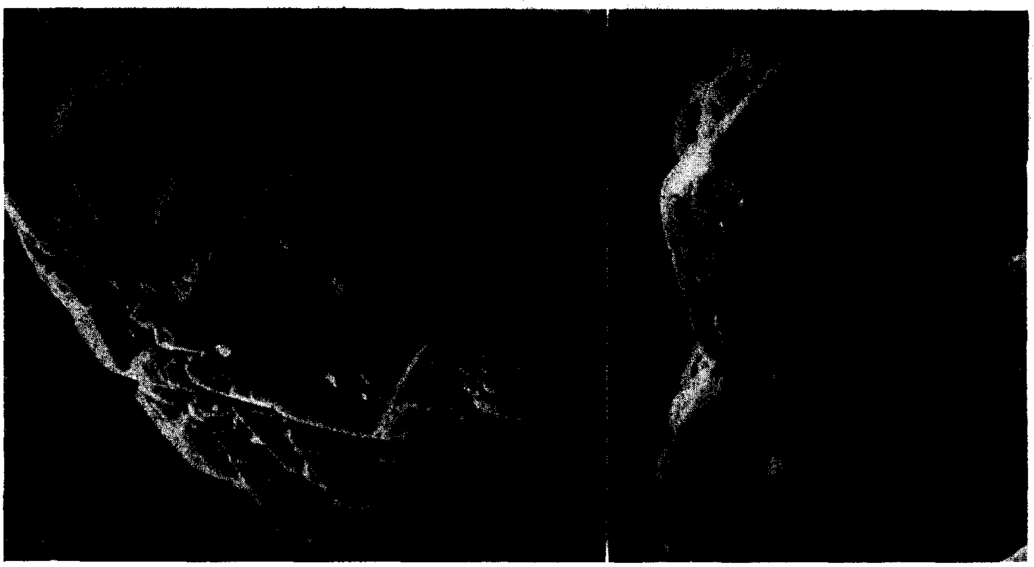


FIG. 1. Electron micrographs of the three gibbsite samples studied: 0.2 μm (A); 1 μm (B); 50–80 μm (C).

tion. Their particle size provides an easy means of designating them. It can be seen that the 50–80 μm sample, an industrial gibbsite, prepared by the Bayer process and provided by the Ugine Company, is made up of grains resulting from the agglomeration of crystals of smaller sizes (5–15 μm), whereas the two other samples (prepared in the laboratories of the Compagnie Pechiney Saint-Gobain (*11*)) consist of flat and distinct crystals for which we may expect a more easily understandable thermal decomposition process. Let us note that a sample similar to our 1 μm gibbsite was studied by Papée and Tertian (*10*) and that the 0.2 μm sample can be compared, from the morphological point of view, with the samples of which MacKenzie and Meldau (*12*) and, more recently, Schoen and Roberson (*13*) reproduce a micrograph.

TABLE 1
SOME CHARACTERISTICS OF THE GIBBSITE SAMPLES STUDIED

Particle size (μm)	Specific surface area ($m^2\ g^{-1}$)	Impurities %		
		Na	Fe	CO_2
50–80	0.14	0.21	0.08	0.21
1	5	0.43	0.37	0.20
0.2	15	0.11	0.02	0.20

Table 1 gives further information on these three samples. Contrary to what may be expected from its high specific surface area, the 0.2 μm sample represents the highest purity.

II. *Experimental Procedure*

1. *Thermoanalytical Methods*

It is worth distinguishing the thermoanalytical methods from the others, not only because they provide a direct means of following continuously the transformation of the sample during the thermolysis, but also because they play a determining part in the decomposition mechanism which we intend to study.

a. Constant rate thermal analysis (C.R.T.A.). As far as the thermal decomposition of gibbsite is concerned, we must recall that *the determining influence of pressure* (in the subatmospheric range) *on the structure* of the resulting aluminas was very soon recognized by Stumpf *et al.* (*4*), whereas its influence on the *texture* was pointed out by Papée and Tertian (*10*). For their part, Eyraud and Goton tried to avoid uncontrolled perturbing processes by performing the kinetic study of this thermal decomposition under vacuum (*14*). Finally, *the influence of the heating rate on the texture and structure* of the resulting aluminas was noticed by Blanchin *et al.* (*15*) and emphasized by Trambouze *et al.* (*16*).

These observations led us to the choice of a thermoanalytical method allowing one at the same time:

to work under a vacuum or under a low water vapor pressure which would be effectively kept at a *constant and known value in the close vicinity of the sample* (this is a specially critical requirement when the thermal decomposition of micron-size samples has to be carried out under vacuum);

to lower to a negligible extent the pressure and temperature gradients within the sample (the mass of which usually lies between 0.5 and 1 g in order to allow subsequent characterizations by other techniques);

to stop the thermolysis precisely at the desired percentage of decomposition and to carry out gas adsorption measurements without at any time exposing the sample to air.

With this object, we have made use of a Constant Rate Thermal Analysis apparatus (C.R.T.A.). It allows (*17*), by its principle, to control at the desired value both the water vapor pressure in the close vicinity of the sample (for pressures ranging between 2×10^{-3} and 20 Torr) and the total decomposition rate (in order to extend, at will, the duration of the complete decomposition over periods of time ranging between one and several hundred hours).

In the case of the two micron-size samples it is no longer necessary, with this method, to set up the vacuum through a glass-frit or through a glass wool pad both of which alter considerably the estimate of pressure and never allow pressures lower than 0.1 Torr to be maintained *during* the decomposition itself. Now, as Papée and Tertian have pointed out (*10*) and as we shall see in a more detailed manner in a forthcoming paper, the nature of the resulting aluminas is not so much dependent on the final pressure (or on the final vacuum, which can be fairly good) than on the pressure around the sample *during* its decomposition. Therefore, this latter pressure is the one which must be measured and controlled.

b. Multicouple differential scanning calorimetry. For the experiments carried out under atmospheric pressure, we made use of a Tian–Calvet calorimeter (*18*), in the same way as Calvet *et al.* have followed the thermal decomposition of several alumina gels and of various boehmite samples (*19*).

The sample mass was always close to 0.7 g and the heating rate was close to 0.3 K min^{-1}.

In the discussion, we shall also mention a calorimetric measurement carried out under low pressure and at constant decomposition rate, by making simultaneous use of constant rate thermal analysis and of multicouple scanning calorimetry, a procedure described elsewhere (*20*).

c. Thermogravimetry (T.G.) and Differential Thermal Analysis (D.T.A.). A Mettler thermoanalyzer was used for simultaneous T.G.–D.T.A. experiments under atmospheric pressure and under vacuum.

2. *Characterization of the Samples*

a. Measurement of specific surface areas by gas adsorption. The volumetric apparatus used for the nitrogen adsorption measurements at 77 K was described elsewhere (*21*). Krypton adsorption was followed with a simple volumetric apparatus including a dosing device and a McLeod gauge.

b. Characterization of crystalline phases by X ray spectrography. The powder diagrams were obtained, at room temperature, with copper $K\alpha$ radiation either photographically (Philips PW 1008 generator and camera) or by counting (C.G.R. diffractometer).

c. Electron-microscope observations. The gibbsite samples, previously brought into suspension in acetone, were sprayed on a carbon film covering the microscope grid (JEM 5 Y). Use was also made of a Cambridge "Stereoscan" scanning microscope.

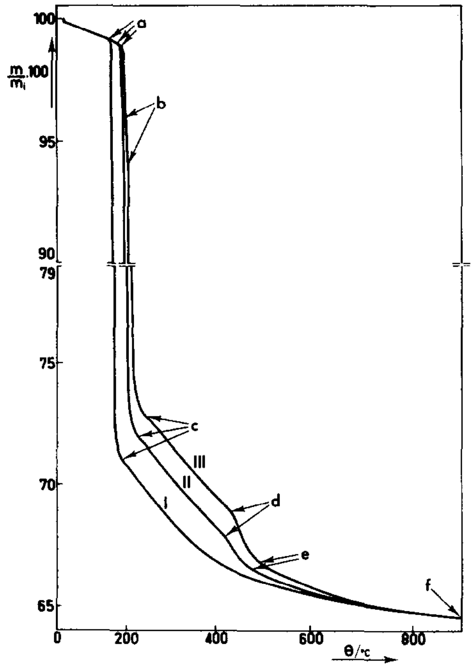


FIG. 2. Influence of pressure: constant rate thermal analysis (C.R.T.A.) curves recorded for the 1 μm gibbsite sample (decomposition rate: 16 mg h^{-1}; initial mass m_i: 1.4 g). Curve I: $P = 20$ mTorr; curve II: $P = 1$ Torr; curve III: $P = 5$ Torr.

B. EXPERIMENTAL RESULTS

I. *Influence of Low Water Pressures on the Boehmite Formation*

Figure 2 shows two characteristic thermoanalytical curves obtained with the C.R.T.A. apparatus for the 1 μm sample. These curves must be considered to be similar to T.G. curves, since they give the mass loss as a function of temperature. The only difference is that, in addition, the decomposition rate is kept constant (16 mg h^{-1} for samples weighing initially 1.4 g) while the residual pressure is controlled; curve I was recorded for a water vapor pressure of 2×10^{-2} Torr. One can notice successively the evolution of physisorbed water (this sample has a specific surface area of 5 m^2 g^{-1}), then the practically isothermal decomposition of gibbsite (part *ac*) and finally the progressive dehydration and transformation of the ρ transition alumina previously formed (part *cf*). This curve is not very different from those obtained by T.G. for micron-size gibbsite (Papée and Tertian (*10*) or Brindley and Choe (*22*)). On the other hand, curves II and III, which were recorded, respectively, for a water vapor pressure of 1 and 5 Torr, do not fit well with observations reported in previous publications. Indeed, part *de*, as well as part *ab*, does not appear on curve I. It points out the thermal decomposition at about 450°C of a boehmitic phase which we easily detect by X rays. The length of part *de* provides a means of determining (in an approximate way which will nevertheless be enough for our discussion) the amount of boehmite which decomposes, that is to say which was formed

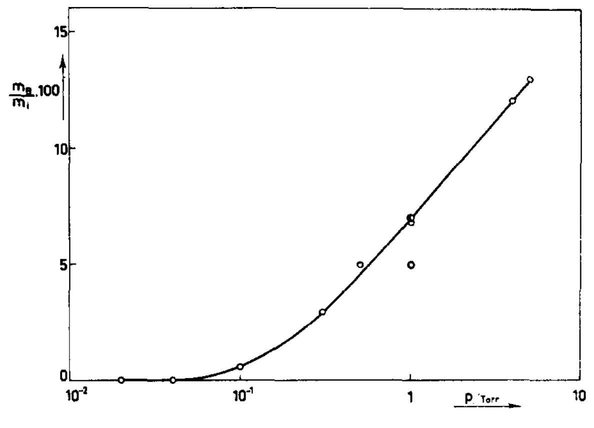


FIG. 3. Percentage of boehmite (in percent of the initial mass m_i of the sample) produced in the 1 μm gibbsite sample, as a function of water vapor pressure ○: from the constant rate thermal analysis curves, ◐: from X-ray spectrography, ○: from calorimetric measurement.

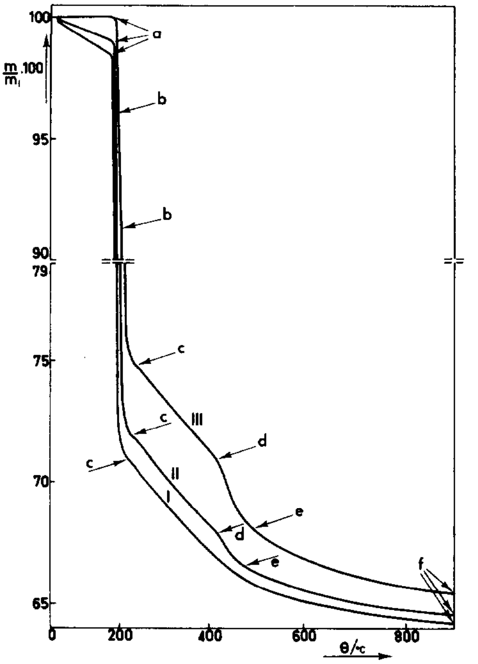


FIG. 4. Influence of grain size: constant rate thermal analysis (C.R.T.A.) curves recorded with: $P_{H_2O} = 1$ Torr; decomposition rate: 16 mg h^{-1}; initial mass m_i of gibbsite: 1.4 g; grain size: 0.2 μm (curve I); 1 μm (curve II); 50–80 μm (curve III).

previously under given conditions of pressure. The results of such a determination of the amount of boehmite formed under pressures lower than 5 Torr have been plotted in Fig. 3. As a check, results obtained from X-ray spectrography and from calorimetry are also plotted. The lowest value, obtained by calorimetry, results probably from the choice of the reference sample (pure boehmite) the hydration of which as well as the porosity are not necessarily identical to those of the boehmitic phase scattered in our partially decomposed gibbsite samples.

II. *Influence of Particle Size upon the Boehmite Formation*

The three C.R.T.A. curves plotted in Fig. 4 were obtained under the same conditions of water vapor pressure (1 Torr) and of decomposition rate (16 mg h^{-1}g^{-1}), for a starting mass of sample of 1.4 g. The three samples differ by their particle size. Not detectable in the case of the 0.2 μm sample (curve I), the amount of boehmite formed (denoted by part *de* on the C.R.T.A. curve and checked by X ray diffraction) increases with grain size (curves II and III).

In a simpler manner, but less well defined, this influence of particle size may be shown under higher partial water vapor pressures: it is enough to work under atmospheric pressure, without any air flow. The decomposition reaction can then be followed by scanning calorimetry. The corresponding curves are drawn in Fig. 5. They concern the 0.2 μm sample (curve I), the 1 μm sample (curve II), the 50–80 μm sample (curve III), and a microcrystalline boehmite sample (curve IV) used for calibration. The percentages of boehmite deduced in this way are shown in the figure itself. These results must be compared with those obtained by D.T.A. by de Boer *et al.* (*23*) or by Lodding (*24*) in the case of a coarse gibbsite submitted to a more or less extended wet-grinding. Nevertheless, because of the low heating rate which is possible with the high sensitivity scanning calorimetry (0.3 K min^{-1} instead of 8 K min^{-1} used by Lodding (*24*)) we are almost free of the problem of the base line shift which appears in D.T.A. work (due to change in heat capacity during decomposition) and decreases the accuracy of the estimation.

III. *Texture Changes*

It will be enough, for our reasoning, to give the texture changes corresponding to part *ab* on the curves of Figs. 2 and 4. We note that *for the 1 μm sample,* whatever the amount of boehmite formed during the C.R.T.A. experiment may be:

the specific surface area measured, at point *b*, by nitrogen adsorption, lies between 5 and 7 m^{2}g^{-1}. This result fits with those obtained by Papée and Tertian (*10*) and by de Boer *et al.* (*25*) in the case of coarse gibbsite;

the electron micrographs do not show any detectable change. No cracks are noticeable on the surface of the crystals at the end of this first decomposition step.

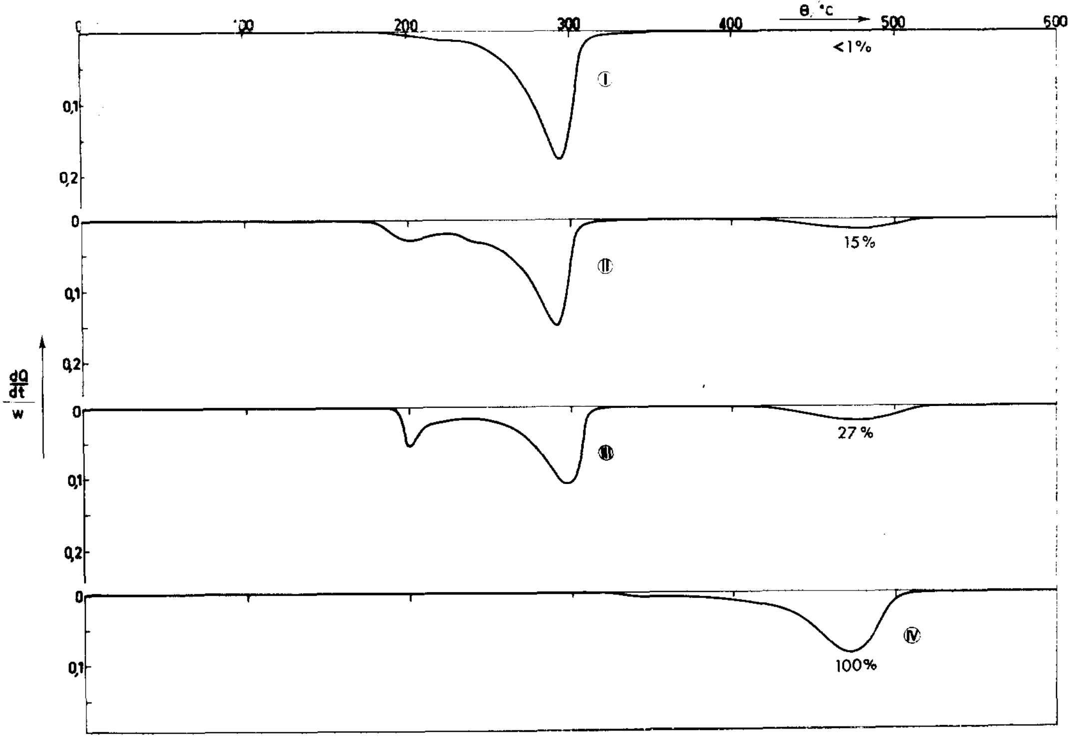


FIG. 5. Scanning calorimetry curves (heating rate = 0.3 K min^{-1}, in air) for: gibbsite 0.2 μm (curve I); gibbsite 1 μm (curve II); gibbsite 50–80 μm (curve III); boehmite 0.3–3 μm (curve IV).

IV. *Results Obtained from Simultaneous T.G. and D.T.A.*

For all our samples we could observe (*26*):

(1) a fairly good synchronism between the T.G. and D.T.A. signals;

(2) a loss of mass, corresponding to the first D.T.A. endotherm (assigned to boehmite formation), which is equal, within the acceptable error (±15%, due to errors in estimating the beginning and the end of the D.T.A. peak), to twice the loss of mass measured during the recording of the third D.T.A. peak (assigned to boehmite decomposition).

C. DISCUSSION

The formation of boehmite within micron-size gibbsite crystals is not generally accepted under atmospheric or subatmospheric pressure. Depending on the authors, this transformation is thought to be either nonexistent (Papée and Tertian (*10*)), very weak (Brindley and Choe (*22*)), detectable but difficult to estimate (Courtial and Trambouze (*27*)) or total (Beretka and Ridge (*9*)).

Presumably, the (unknown) differences in the impurity content of the samples used can partially explain these discrepancies. Nevertheless, we think that only differences in the conditions of the thermolysis, the particle size of the samples and the sensitivity of the analytical methods would be enough to account for that diversity. We shall now discuss this in detail.

Let us first sum up the experimental results from which our discussion will start:

boehmite can appear in micron-size gibbsite crystals;

it can be formed in a non-negligible proportion (5%) at as low an external water vapor pressure as 0.5 Torr;

the loss of water during this first step is not accompanied by the formation of a porosity accessible to nitrogen (observed too in (*10*) and (*25*)).

On the other hand, the problems to be solved are the following:

How can one explain the influence of low water vapor pressures upon the gibbsite → boehmite transformation which is known to require usually hydrothermal conditions, that is to say a high pressure?

What factors can limit and determine the amount of boehmite formed?

What factors are responsible for the transition from the first step (formation of boehmite) to the second one (formation of transition alumina)?

As a corollary of the former question, do we have to consider an influence of one step upon the other, or can they be thought to be independent from each other?

Of course, the model which we propose as an answer to these various questions makes a wide use of those which have been previously put forward, especially by de Boer *et al.* (*7*) and by Papée and Tertian (*10*), but tries at the same time either to harmonize them, or to make them more explicit. We shall consider successively the reasons of boehmite formation and then the reasons for the incomplete character of that first step and of the transition towards the second.

I. *Formation of Boehmite in the Gibbsite Crystal*

First of all, we shall agree (because this may be the only point generally accepted since it has been proposed by de Boer *et al.* (*7*) and by Papée *et al.* (*28*)) that the transformation of gibbsite into boehmite requires hydrothermal conditions which can be, even in a powder, locally fulfilled. According to Papée and Tertian (*10, 28*), these conditions are fulfilled inside each grain of coarse gibbsite acting like an autoclave, but this is no longer possible as soon as the gibbsite crystals become distinct and free. Now, from our experiments, we must conclude that, even in the latter case, boehmite can be formed. Therefore we think that internal hydrothermal conditions are fulfilled even in the case of a micron-size crystal. We observed this first step at temperatures ranging from 180 to 205°C. Let us recall that only above 155°C, under prolonged hydrothermal conditions (85 hours in the presence of saturated water vapor), is the transformation gibbsite → boehmite complete (Laubengayer and Weiz (*29*)).

We shall, therefore, assume that boehmite can be formed *in the interior of the crystal.* Now we have noticed the synchronism between the D.T.A. and T.G. signals. This means that the excess water escapes out of the crystal, from the very beginning of the transformation. In order to explain this, we must refer to the structure of the gibbsite crystal, as published by Megaw (*30*) or, more recently, by Sasvari *et al.* (*31*) and Saalfeld (*32*).

From the latter, we reproduce the three projections of Fig. 6. One can see that the water molecules—or the hydroxyls—may follow two different paths:

(a) the cleavage planes, parallel to the [001] face of the crystal,

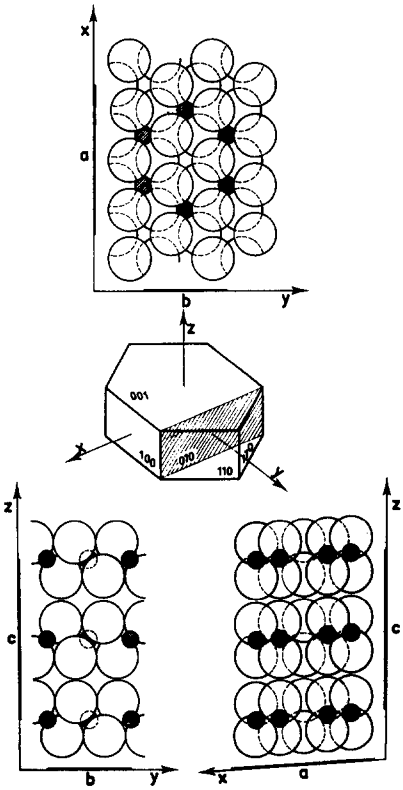


FIG. 6. Crystalline structure of gibbsite, after Saalfeld (*32*).

(b) the "structural channels," perpendicular to the former planes. These channels arise from the fact that in their own layer the Al atoms only occupy two possible sites among three, and that the sites left vacant are superimposed from one composite layer to the next. We must keep in mind that these structural channels are lined with hydroxyls only and that in spite of their very narrow aperture (diameter $<$ 1 Å), they can allow the hydroxyls to migrate step by step, by mutual displacement (*33*).

We have no reasons, now, to exclude one of those possibilities. In both cases, the hydrothermal conditions may be maintained within the crystal, thanks to the combined action of a difficult migration of water (either along the structural channels or along the cleavage planes) and of a difficult desorption from the openings of the channels or from the edges of the cleavage planes. We must indeed appeal to a desorption mechanism to explain the influence of low water vapor pressures on the development of the first step: the starting temperature of that step (point *a* on the curves of Figs. 2 and 4) varies (for a mass of 1.4 g of 1 μm gibbsite decomposed at a rate of 16 mg h^{-1}) from 172 to 180°C when the vapor pressure varies from 0.1 to 1 Torr.

In both cases also the migration may occur by mutual displacement of structural water, which would be consistent with Steggerda's experiments (*34*): this author noticed indeed that as long as gibbsite decomposes into boehmite the porous system obtained is only available to water molecules and not to other adsorbates like ethanol, carbon tetrachloride, nitrogen, butane or even helium.

Let us now come back to some aspects of the preceding model.

1. *Localization of the Boehmitic Phase*

We have assumed that the boehmitic phase was formed in the interior of the crystal and progressed towards the external faces of the crystal. Now, to explain the lowering of the decomposition rate which is observed by D.T.A. at the end of the first step (and which is responsible for the gibbsite "dehydroxylation fork"), Lodding has recently suggested that boehmite could form an impervious layer around the unreacted gibbsite grain or "crystallite" (*24*).

We think nevertheless that such a picture does not explain why it is that the higher the starting gibbsite specific surface area, the lower is the amount of boehmite formed, nor why the transformation into boehmite is not complete.

2. *Lacunar Structure of the Boehmitic Phase*

The advance of the boehmitic phase (density 3.02 g cm^{-3} according to (*29*)) inside a gibbsite of lower density (2.42) easily accounts for the formation of gaps which are naturally filled with water: such an occluded water, inside the boehmitic phase, could be detected by one of us (*35*) by nuclear magnetic resonance.

3. *Formation of Boehmite in a Polycrystalline Grain*

Up to now, we have mainly considered the case of the distinct and free gibbsite crystal. The case of the polycrystalline grain (which is that of the Bayer process gibbsite, like our 50–80 μm sample) is not so simple, on account of the irregular shape of the grain. It can nevertheless be interpreted by the same mechanism as formerly, inside the elementary crystal, with no need of supposing a good cohesion or a good tightness of the grain.

II. *Completion of the Boehmite Formation and Beginning of the Transition Alumina Formation*

In order to make this part of the discussion clearer, we shall start by giving our scheme for the mechanism. Afterwards, we shall submit it to a critical examination.

We suppose that the completion of boehmite formation is due to a lowering of the intracrystalline pressure. This lowering can originate from two reasons:

(a) from the appearance of cracks in the crystal, resulting from a quick reaction;

(b) from the thinning down of the gibbsite shell, itself resulting both from the advance of the boehmitic phase from the inner to the outer parts of the crystal, and from the beginning of a surface decomposition of gibbsite according to the process of the second step.

As for the transition from the first step (boehmite formation) to the second one (transition alumina formation), we think it obeys simple kinetic factors in such a way that the beginning of the second step can arise either from a texture change or from an increase in temperature, without involving any inconsistency between these two possibilities.

Let us now examine this scheme in more detail.

1. *Completion of the First Step by Formation of Cracks*

This is likely to be the more general case since it concerns a thermolysis carried out without special care. It was well studied by Papée and Tertian (*10*). During the course of a thermolysis carried out at 200°C (under atmospheric pressure), these authors observe indeed the succession of the two steps. Moreover, for their coarse gibbsite sample (50–80 μm) they note a coincidence between the beginning of the second step and the beginning of the surface area increase. From this they reasonably infer that the transition from the first to the second step is not determined by a temperature threshold (which is not overstepped here) but by the texture development of the sample. That development of the texture may be considered as a consequence of the water vapor excess pressure accompanying the boehmite formation and disaggregating the gibbsite grains.

We think it useful to add the following comments:

(a) The water vapor excess pressure can also act at the scale of the elementary crystal, producing cleavages in the (001) plane (the gibbsite composite layers being only weakly linked together (*30*) by hydrogen bonds).

(b) The second step process reaches an appreciable rate as soon as the reaction interface has increased to an appreciable extent.

(c) In the case of constant heating rate thermolysis, the simultaneity of the beginning of the second step and of the surface area increase does not allow one to determine which of these phenomena must be considered as the cause of the other (the temperature rise adding here an extra parameter).

(d) The existence, in the D.T.A. trace, of a more or less distinct peak for each step (the gibbsite dehydroxylation fork of Lodding (*24*)) could mean, as de Boer *et al.* (*7*) suggest, that the second step cannot take place unless a temperature threshold is reached, but actually, even for the very low heating rates we have chosen (0.3 K min^{-1}, cf., Fig. 5), it is never possible to separate *completely* these two peaks. Therefore, at the temperature which corresponds to the end of the first step, the second step already takes place at an appreciable rate; this is why the isothermal experiment of Papée and Tertian was possible. But the maximum rate is not obtained, for the two steps, at the same temperature; this is shown by the D.T.A. fork.

(e) When the gibbsite sample is submitted to C.R.T.A., the transition from the first step to the second one is gradual. This is shown by the calorimetric curve recorded during a simultaneous experiment of C.R.T.A. and scanning calorimetry. We published such a curve elsewhere (*20, 26*). It gives us directly the differential enthalpy of decomposition as a function of the mass lost. The "D.T.A. fork" is no longer detectable. The differential enthalpy of decomposition of gibbsite first has a constant value of (50 ± 2) kJ $\text{mol}_{\text{H}_2\text{O}}^{-1}$ (first step) and then slowly increases up to (77.0 ± 3.5) kJ $\text{mol}_{\text{H}_2\text{O}}^{-1}$ (plateau corresponding to second step).

2. *Completion of the First Step by Thinning down the Gibbsite Shell*

This second possibility was first suggested by Steggerda (*34*). It can only be observed in the case when the thermolysis is carried out in such a slow and progressive way as to avoid the formation of cracks which would bring us back to the case described in the former section. Those conditions are precisely fulfilled by C.R.T.A. The C.R.T.A. traces (Figs. 2 and 4) offer a good means of following that mechanism.

Part *ab*. The first step is developing alone but, as the boehmitic phase is formed, the gibbsite shell becomes thinner, the internal pressure is lowered and, in order to keep the decomposition rate constant, a temperature rise is necessary. (This decrease of the internal pressure is a result of diffusion of water through the gibbsite shell, causing a depletion of the liquid water in the holes.) It follows that part *ab* is inclined (undoubtedly, the word "pressure" which usually covers a macroscopic notion is not very proper at the microscopic scale which is considered here; nevertheless, we make use of it in consequence of the analogy which we assume between the formation of boehmite in the middle of the crystal and its formation in a hydrothermal bomb).

Point *b*. Here, a temperature is reached at which, *under a given preset working pressure* (this point will be developed in a forthcoming paper), the second step process can reach such a rate as to supplant the first one. The latter comes to an end because:

the second step goes on without the temperature rise which would be necessary to keep the first step process at a constant rate;

the advance of the second step reduces the thickness of the remaining gibbsite shell.

To finish, let us point out some consequences of the preceding decomposition scheme.

a. Influence of particle size. A large size delays the time when boehmite is no longer formed and increases, therefore, the final amount of boehmite.

b. Influence of water vapor pressure. Water vapor not only acts directly upon boehmite formation (on account of a difficult desorption from the opening of structural micropores) but it acts, too, in an indirect way. Its influence on the rate of the second step process is such as to raise the temperature at which the desired rate is reached; the time when the transition towards the second step takes place is, therefore, delayed and the amount of boehmite formed is increased (Fig. 2, part *ab* of the curves II and III).

c. Influence of heating rate. The influence of heating rate upon the percentage of boehmite formed was studied by Courtial *et al.* (*36*) under atmospheric pressure. Their conclusion is that extremely low heating rates enhance the formation of boehmite. It fits with our scheme since we understand easily that, by avoiding the appearance of cracks, one delays the termination of the first step.

d. Absence of boehmite in some circumstances. It follows from the foregoing that, by lowering the external pressure, one lowers the temperature T_b corresponding to point *b* (Fig. 2). When the crystal is small enough (as with our 1 μm gibbsite sample) it is possible to choose, at will, a pressure such as to have point *b* coincident with point *a*; the first step is then cancelled out and no boehmite (or traces only) is formed (curve I, cf., Fig. 2). This result is not consistent with those of Beretka and Ridge (*9*) who observed that, under vacuum, the transformation of a 5–15 μm gibbsite sample into boehmite is complete. These authors recognized indeed the X ray spectra of boehmite in a sample previously heated under vacuum at 250°C and corresponding approximately to the formula $Al_2O_3 \cdot H_2O$. Now one knows that the presence of ρ-alumina, even at a high percentage (75%), leaves untouched the boehmite spectra (*10, 37*) and that the water content of a ρ-alumina is not well defined. Therefore we are inclined to think that if Beretka and Ridge are certain of the boehmite formation, they can hardly affirm that only boehmite has been formed.

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