SHORT COMMUNICATIONS

Proton Magnetic Resonance Absorption of Aluminum Hydroxides and of their Thermal Dehydration-Products

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The phase transformations occurring in the thermal decomposition of the alumina trihydrate belong, as of old, to the subject of extensive researches. The present authors have now tried to study the thermal dehydration of alumina trihydrate by means of a method of proton magnetic resonance absorption**.

The starting material here employed was a bayerite prepared by a chemical reaction of an aluminum chloride solution with an aqueous ammonia. Each specimen was subjected to the corresponding heating of this starting material during 3 hr. in the air at 100°, 200°, 220°, 250°, 300°, 450° and 600°C, respectively. They were sealed in the evacuated glass tubes which were pumped out to a high vacuum, either at room temperature during 12 hr. or at 110°C during 6 hr., the latter having the purpose of an after-treatment. We call the former group as "a-series" and the latter one as "b-series".

For the NMR measurements, we have used the a.c. modulation technique of the magnetic field at the d.c. magnetic field of about 3100 gauss. The detecting apparatus has the ordinary constitution, which is composed of an autodyne oscillator, an audio-frequency amplifier, a lockin-amplifier and a recording milliammeter.

The measurements of the proton magnetic resonance were also made in the well-known definite hydrargillite, bayerite, böhmite and natural diaspore, respectively. Some reproductions of the experimental line shapes of the proton resonances are shown in Figs. 1 and 2.

As is seen in Fig. 1, the line shapes of the hydrargillite and of the bayerite or the starting material may be presumably understood as being composed of two parts: one is situated at the center with the narrower width and another is of very broad at both sides of it. The line shape of the böhmite shows the signal of the three spin type, while that of the

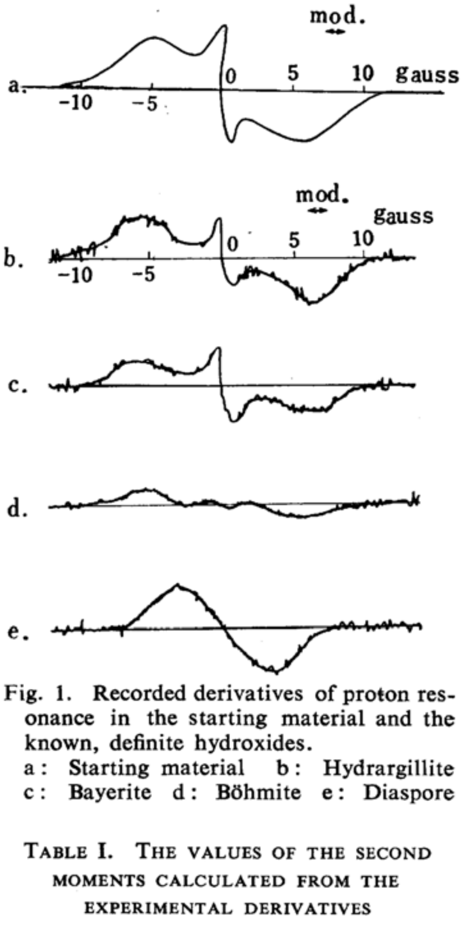

Fig. 1. Recorded derivatives of proton resonance in the starting material and the known, definite hydroxides.
a: Starting material b: Hydrargillite
c: Bayerite d: Böhmite e: Diaspore

TABLE I. THE VALUES OF THE SECOND MOMENTS CALCULATED FROM THE EXPERIMENTAL DERIVATIVES

Specimen	Second moment (in gauss^2)
Starting material	12.9
Bayerite	13.1
Hydrargillite	15.2
Böhmite	14.0
Diaspore	6.3
Dehydrated at 100°C-(b)	13.4
〃 at 200°C-(b)	13.7
〃 at 220°C-(b)	14.0
〃 at 250°C-(b)	8.3
〃 at 300°C-(b)	6.8
〃 at 450°C-(b)	4.3
〃 at 600°C-(b)	3.0

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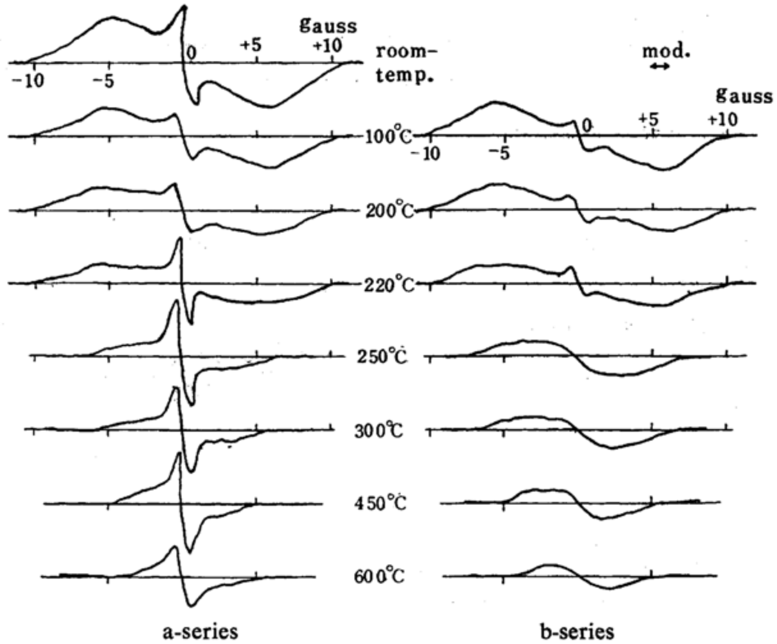

Fig. 2. Recorded derivatives of proton resonance in the a- and b-series—(without and with the after-treatments, in vacuo, 110°C).

diaspore shows the single and narrow line. The values of the second moments calculated from the experimental derivative curves are shown in Table I.

The line shapes of each specimen dehydrated at 100° and 200°C are both similar to that of the starting material. The amplitudes of the central components observed for these line shapes are somewhat reduced by the thermal after-treatment, as in a high vacuum pumping at 110°C, but they yet never disappear by such a treatment. Nevertheless, the line shapes of the specimens dehydrated at about 220°C and higher make quite a difference from above two specimens and the height of the central peaks in these line shapes considerably increases. It is noteworthy that these central peaks, however, disappear by the such after-treatment, as in a high vacuum pumping at 110°C. These interesting behaviors can be seen in Fig. 2. Therefore, we are to suppose that these central peaks in the latter case originate from the water-molecules which are adsorbed by the decomposed products and are in the thermal motion.

Based upon the above experimental fact, the following conclusions can be drawn:

1) The decomposition of this starting material does not occur till the thermal dehydration temperature of about 200°C. This is ascertained in our NMR experiments.

2) The sudden and considerable variation of the central part observed in the line shapes at an about 220°C and higher, seems to show that the first dehydration process of this starting material brings forth an active lower hydroxide, exhibiting very high activity for an adsorption.

3) The gradual decrease of the line width occurring in the range from about 250 to 600°C might be regarded as a result due to the changing of the mixed ratio of the lower hydroxide and alumina phases.

These conclusions will be ascertained by the additional experiment by means of X-ray diffraction method which is in progress in our laboratory.

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