Proton Magnetic Resonance Studies on the Thermally Dehydrated Products of Alumina Trihydrate

By Tatsuo SAITO

(Received November 19, 1960)

In the previous communications[1-2], the proton magnetic resonance absorption spectra of thermally dehydrated products have been studied to obtain information about the mechanism of the thermal decomposition of bayerite. In the present paper, the author has tried to investigate the rehydration of the thermally dehydrated product of alumina trihydrate by means of the proton magnetic resonance absorption spectra.

The rehydration of the thermal decomposition product of alumina trihydrate has recently been studied by many investigators[3-6]. The present author has examined the rehydration of the hydrous alumina dehydrated at various temperatures in high vacuum system. The rehydration was carried out under the vapor pressure of saturated water vapor at room temperature in the vacuum system.

Experimental

Starting Material.—The alumina trihydrate, bayerite, was prepared by a chemical reaction of 1 N aluminum chloride solution with a small excess of 1 N ammonium hydroxide solution at room temperature. The resulting precipitate was washed by decantation for about 10 days till it was free from chloride and was then dried at 50°C for 24 hr. This starting material was checked by X-ray diffraction study and it was found that the resulting diffraction diagram was the same as that of bayerite, as shown in Fig. 1.

Apparatus and Procedure.—The NMR measurements were performed using the modulation technique described by Bloembergen, Purcell and Pound[7]. The detecting apparatus has the ordinary constitution, which is composed of an r-f oscillator, an r-f amplifier, a detector, an audio-frequency amplifier, a lock-in amplifier and a recorder. More detailed reviews of this apparatus may be found in the article by Yano[8].

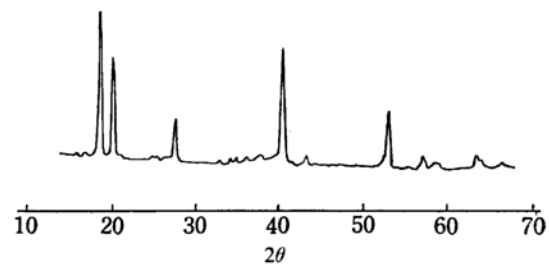

Fig. 1. X-Ray diffraction diagram of the starting material.

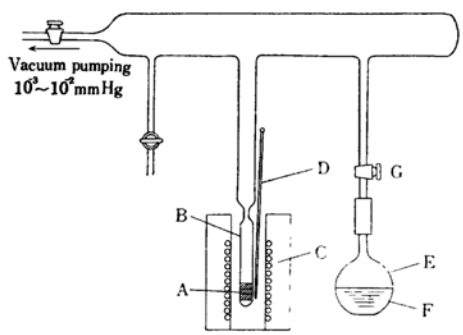

Fig. 2. Apparatus used to prepare the specimen for the NMR measurement.
A; Sample cake (dia. 8mm.)
B; Resonance sample tube
C; Electric furnace
D; Thermometer or thermocouple
E; Flask (100 cc.)
F; Distilled water in evacuated flask
G; Cock

1) T. Hagiwara and T. Saito, This Bulletin, **33**, 1463 (1960).
2) T. Saito, ibid., **33**, 1626 (1960).
3) M. K. B. Day and V. J. Hill, *Nature*, **170**, 539 (1952); *J. Phys. Chem.*, **57**, 946 (1953).
4) R. Tertian and D. Papée, *Compt. rend.*, **236**, 1565 (1953); **238**, 98 (1954); **241**, 1575 (1955).
5) B. Imelik, ibid., **233**, 1284 (1951).
6) H. Thibon and E. Calvet, ibid., **239**, 1133 (1954).
7) N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, **73**, 679 (1948).
8) S. Yano, *J. Phys. Soc. Japan*, **14**, 942 (1959).

Each specimen used for the NMR measurement was prepared by the device of vacuum system illustrated in Fig. 2.

For the preparation of each specimen of thermally dehydrated product in vacuo, about 2 g. of the starting material was pressed into small cakes and they were put into the resonance sample tube which was connected to the high vacuum system. Then, each resonance sample tube was evacuated and heated from outside by the electric furnace for 3 hr. and it was then sealed off. The dehydration temperature was 100, 150, 200, 250, 300, 400 and 500°C, respectively.

For the preparation of rehydration-specimens, each sample after the treatment of the thermal dehydration in vacuo was immediately exposed at room temperature for 15 hr. to the saturated water vapor which entered through the cock (G) from the flask (E) (shown in Fig. 2).

Then, each sample tube containing this rehydrated specimen was pumped out to a high vacuum, either at room temperature during 12 hr. or at 110°C during 6 hr. and it was then sealed off.

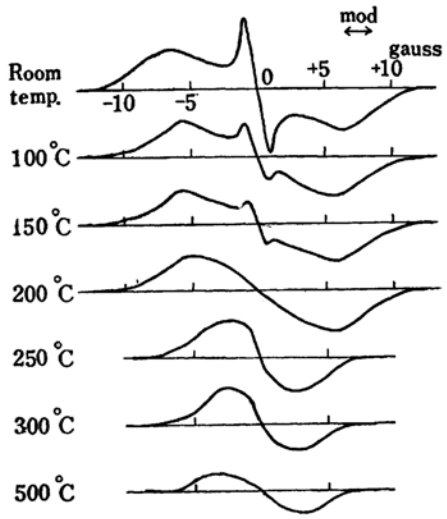

Fig. 3. Recorded derivatives of proton resonance in the thermal dehydration products in vacuo.

Results and Discussion

Thermal Dehydration in Vacuo.—The derivative curves of the proton resonance absorption taken on the thermally dehydrated products in vacuo are shown in Fig. 3. The line shapes obtained from the specimens dehydrated at 100 and 150°C are both similar to that of the starting material, but the intensity of center peaks observed for these line shapes somewhat decreases with the rise of temperature. The line shape obtained from the specimen at 200°C has no central component though its line width is almost equal to that obtained from the specimen at 150°C.

This means that at the thermal dehydration till the temperature reaches 200°C, the structure water is not released but the adsorbed water

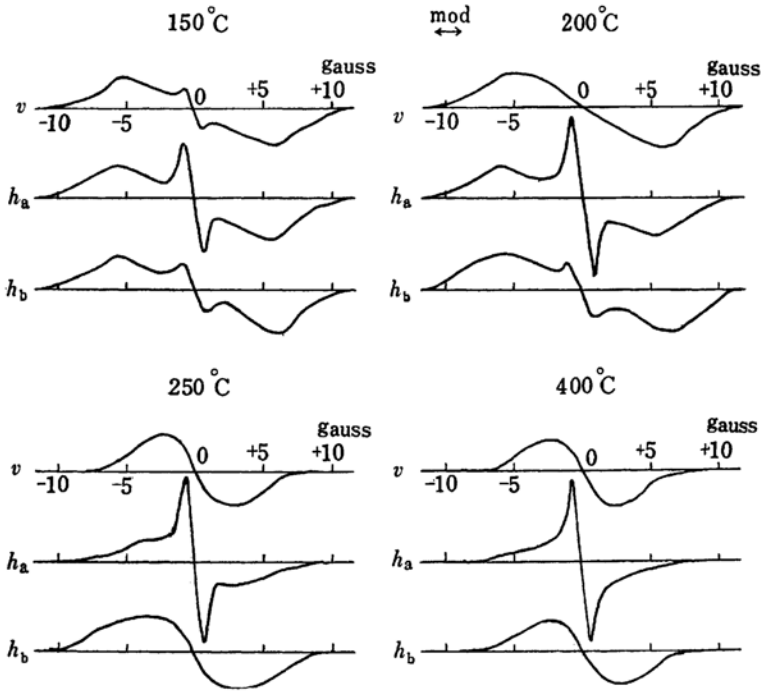

Fig. 4. Recorded derivatives of proton resonance in the thermal dehydration products in vacuo and their rehydrated samples.

vaporizes from the compound with the rise of temperature.

However, as shown in Fig. 3, the line width obtained from the specimen at 250°C suddenly becomes narrow and then the specimens at 300 and 500°C have also the same narrow width. This means that the starting material directly decomposes to the hydrous alumina at 200～250°C.

Rehydration of Thermally Dehydrated Products in Vacuo.—The NMR measurements were carried out on the specimens prepared by the rehydration of the thermally dehydrated products of bayerite in vacuo. The experimental derivative curves obtained from these measurements are shown in Fig. 4.

In Fig. 4, "v" is the recorded derivative of dehydrated product in vacuo at each temperature, and both "h_a" and "h_b" are the recorded derivatives of the rehydrated sample of the above dehydration-product. In this case, "h_a" shows the rehydrated sample having the after-treatment of a high vacuum pumping at room temperature during 12 hr. and "h_b" shows one having the after-treatment of a high vacuum pumping at 110°C during 6 hr.

As is seen in Fig. 4, the line shape of "h_a-series" has a sharp and intensive central component, but in the line shape of "h_b-series", the center peak observed for this line shape remarkably reduces in its intensity as compared with that of "h_a-series" or disappears. At 150°C, the line shape of the derivative "h_b" is the same as that of "v", but at 200°C, the line shape of the derivative "h_b" shows the difference from that of "v". This means that on the dehydration in vacuo at 200°C, the starting material partially decomposes to hydrous alumina and then this decomposed product is rehydrated by water vapor to aluminum hydroxide. At 250°C, the line width of the derivative "h_b" becomes larger than that of "v" and at 400°C, the line width of the derivative "h_b" is the same as that of "v".

The second moments calculated from these experimental derivative curves of "v-series" and "h_b-series" are shown in Table I and the variation of these values of second moments plotted as the function of the temperature are shown in Fig. 5.

TABLE I. THE VALUES OF THE SECOND MOMENTS CALCULATED FROM THE EXPERIMENTAL DERIVATIVE CURVES

Dehydration temp., °C	Thermally vacuum dehydration series, gauss^2	Rehydration series "h_b-series" gauss^2
room temp.	13.6	
100	13.4	
150	13.3	14.0
200	12.1	13.9
250	4.8±0.5	8.2±0.3
300	4.3±0.2	5.8±0.3
400	4.5	4.6±0.2
500	4.1	4.4

As is seen in Fig. 5, the second moments of the thermal dehydration series in vacuo decrease from the value of 13～14 gauss^2 to that of 4～5 gauss^2 suddenly at 250°C and this value of 4～5 gauss^2 constantly continues till 500°C. In the variation curve of the second moments of the rehydration series—"h_b-series", the values of second moments below 200°C

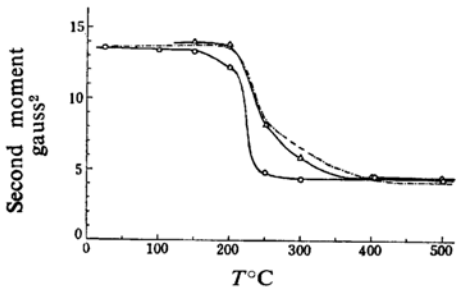

Fig. 5. Variation of the second moments with the temperature in the thermally vacuum-dehydration series and the rehydration series—"h_b-series"
○—○; Thermally vacuum-dehydration series
△—△; Rehydration series—"h_b-series"
·—·—; Thermal dehydration series in the air

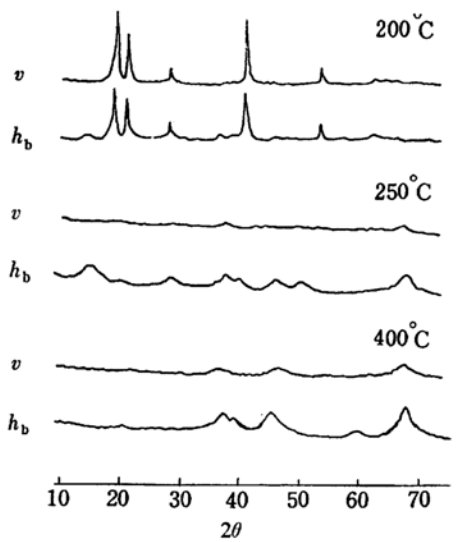

Fig. 6. X-Ray diffraction diagrams of the samples in the thermally vacuum-dehydration series and in the rehydration series—"h_b-series".
v; Thermally vacuum-dehydration series
h_b; Rehydration series—"h_b-series"

are about 13～14 gauss[2] and in the range from 200 to 400°C, the values gradually decrease with the rise of temperature. Then, in the range from 400 to 500°C, the second moments become stationary values of 4～5 gauss[2].

The above difference of the variation curve of second moments in the range from 200 to 400°C between "v-series" and "h_b-series" is interpreted as a result due to the formation of aluminum hydroxide by the rehydration of the thermally dehydrated product in vacuo.

This interpretation of the rehydration was ascertained by the X-ray diffraction study of the products. The diffraction diagrams of several specimens obtained in this study are shown in Fig. 6. From these diagrams, it is ascertained that, while the specimen of the thermal dehydration in vacuo at 250°C is crystallographically amorphous, the specimen obtained by the rehydration for the above sample shows a mixed phase of böhmite and η-alumina.

Conclusion

1) The center peak observed for the line shape of the experimental derivative curve of proton resonance in the starting material decreases in its intensity during the thermal dehydration in vacuo at the temperature below 200°C, but it does not disappear till 150°C. The author assumes that this center peak shows the existence of the movable water which entered into the crevice of the lump of fine particles or entered into the space of the layer lattice of crystal.

2) On the thermal dehydration series in vacuo, the starting material directly decomposes to the hydrous alumina at the temperature of 200～250°C and the intermediary product, böhmite, is not found in the specimens at 250 and 300°C. This is ascertained in present NMR experiments.

3) The water which was adsorbed by the rehydration of the thermally dehydrated products in vacuo at 150°C is wholly removed by the treatment of a high vacuum pumping at 110°C.

4) In the rehydrated product of the thermally dehydrated sample in vacuo at 250°C, the adsorbed water of the product changes partially into the structure water and the formation of aluminum hydroxide occurs partially. This is ascertained by the NMR measurements.

5) In the rehydration specimen of the dehydration-product in vacuo at 400°C, the formation of aluminum hydroxide is not observed.

6) It is noteworthy that the variation curve of second moments for the rehydration series—"h_b-series" shows the same figure as the variation curve of second moments for the thermal dehydration series in the air[2].

The author wishes to express his sincere thanks to Dr. Y. Kotera of this Institute for his kind advice. The author also wishes to express his hearty thanks to Professor T. Hagiwara of Hiroshima University for his kind direction and also wishes to express his sincere thanks to Professor T. Sidei and Dr. S. Yano of Kyoto University for their continual guidance and encouragement throughout this study.

Government Chemical Industrial Research Institute, Tokyo
Shibuya-ku, Tokyo