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STUDIES ON THE REACTIONS OF ALUMINIUM OXIDES AND HYDROXIDES

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The hydrothermal and decomposition reactions of differently ground gibbsite and its reaction products were studied. The samples were treated isothermally under hydrothermal conditions or in air, and the products were characterized by thermogravimetry and IR spectroscopy. It was found that the method and duration of grinding and the particle size of the starting gibbsite influenced the reactivity of the gibbsite itself and that of the primary reaction products. In a later step of the reaction sequence (hydrothermal rehydration of γ-alumina), the effects of the differences in the properties of the starting gibbsites were insignificant.

In spite of the fact that the thermal reactions of aluminium hydroxides and oxides have been thoroughly investigated during the past 40 years, contradictory results can be found even in recent publications.

On the basis of a literature review, Paulik and coworkers [1] gave four potential or proposed modes of thermal decomposition of gibbsite:

a. Decomposition via boehmite:

$$\alpha\text{-Al(OH)}_3 \rightarrow \alpha\text{-AlO(OH)} \rightarrow \gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$$

b. Decomposition directly to α-alumina:

$$\alpha\text{-Al(OH)}_3 \rightarrow \chi\text{-Al}_2\text{O}_3 \qquad \kappa\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$$

c. A two-pathway reaction, with the formation of χ-alumina as major and boehmite as minor product:

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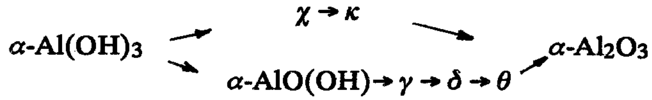
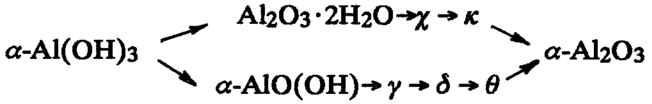


d. A two-pathway reaction yielding $Al_2O_3 \cdot 2H_2O$ as major and boehmite as minor product:



It is well known that boehmite formation is favoured by hydrothermal conditions. Steggerda and Lippens found that, under hydrothermal conditions below 10^7 Pa, the product of gibbsite is boehmite, which is the thermodynamically stable phase up to 300° [2]. Moreover, the results of Buman *et al.* [3] suggest that boehmite formation does not require an atmosphere of saturated water vapour. At 200°, partial boehmite formation took place below 5.2% relative humidity. Boehmite was the only product above this relative humidity.

If gibbsite is heated in air, the ratio of the resulting χ-oxide and boehmite depends on the properties of the sample (origin, particle size and specific surface area) [4, 5]. Starting from the interpretation of de Boer *et al.* [6], a detailed explanation was worked out for the mechanism of reaction fork (c) by Rouquerol *et al.* [7, 8].

Two limiting cases of gibbsite thermal decomposition in air were distinguished by Paulik *et al.* [1]: from a gibbsite consisting of coarse grains, the amount of boehmite in the product may amount to 25%, while no boehmite formation was observed from a natural gibbsite mineral consisting of fine particles. Similar results were obtained by Pokol *et al.* in a study on the kinetics of the isothermal decomposition of gibbsite [9].

If boehmite (formed under hydrothermal conditions) is heated further in air, dehydration to γ-alumina occurs. The temperature of this reaction depends on the degree of crystallinity of the boehmite. A poorly crystalline boehmite was found to decompose at about 450° by Mackenzie *et al.* [10]; the temperature of the reaction was about 100 deg higher for the well-crystallized substance.

Several studies have been carried out on the re-formation of the products of thermal decomposition of gibbsite. A low-temperature γ-alumina containing an amorphous part was rehydrated by Zelentsov and Chertov [11]. Well-crystallized boehmite was obtained at 100-150°; this procedure was suitable for the modification of aluminas prepared from the product of rehydration [11].

The decomposition products of bayerite underwent re-formation to the starting substance on aqueous treatment [12]. Depending on the experimental conditions, gibbsite, pseudoboehmite, nordstrandite and bayerite were obtained from η, γ and χ-aluminas treated with aqueous solutions at between 40 and 130° [13]. The substances obtained in the thermal decomposition of gibbsite in air were processed hydrothermally by the present authors. The final product was found to be boehmite [14].

In the present work, the following reactions of the system were studied:

- the transformation of χ-alumina-boehmite mixtures under hydrothermal circumstances to α-AlO(OH) as the final product;
- the reactions of gibbsite samples after different preliminary mechanical treatments;
- the hydrothermal reaction of γ-alumina.

Experimental

Materials and apparatus

$Al(OH)_3$ (Reanal, pure) was wet and dry-ground in a ceramic ball mill for 6 and 30 hours. A 1% aqueous suspension of the product was separated on a Fritsch Analysette 3 vibration sieve series. The fractions of 20-30 μm and <10 μm particle sizes were used in the experiments. Hydrothermal treatment was carried out in stainless steel vessels, in which the material was in contact with liquid water.

Thermogravimetric curves were measured with a DuPont 951 thermobalance. The infrared spectra of the starting materials and products (in KBr pellets) were recorded on a Nicolet 710 Fourier transform spectrometer with a resolution of ca. 4 cm^{-1}.

1. The gibbsite fractions were kept at 255° for 10 hours to prepare the χ-oxide + boehmite mixtures. The hydrothermal treatment of these mixtures was carried out in the range 120-160°. However, the transformation was fast from 140°, and the conversion *vs.* time curves of different samples were quite similar. The Figures show the conversion curves of mixtures treated at 120 and 130°.

2. The hydrothermal conversion of gibbsite to boehmite was followed at 180, 182 and 190°. At higher temperatures, the conversion curves of the different samples were practically identical.

3. The decomposition of boehmite samples (prepared from gibbsite fractions at 200° during 25 h) to γ-alumina was investigated at 490 and 507°.

4. γ-alumina was prepared from the boehmite samples in a 24-hour isothermal treatment in air at 530°. The hydrothermal reaction of γ-alumina samples was carried out at 180, 190 and 210°.

Results and discussion

Some effect of grinding was observed in the IR spectra of gibbsite samples. The spectrum of the original gibbsite contains five absorption bands in the range of the stretching vibrations of the OH groups. The frequencies are 3621, 3526, 3468, 3394 and 3373 cm^{-1}; the last two bands form a doublet. According to Rouquerol *et al.* [15] and Vivien *et al.* [16], these vibrational modes are characteristic of gibbsite.

Among the ground (mechanically activated) gibbsites, the $< 10\ \mu m$ fraction of material dry-ground for 30 hours exhibited a spectrum different from the others: splitting of the 3526 and 3468 cm^{-1} bands and changes in their intensities were observed (Fig. 1).

Consequently, an effect of grinding on the reactivity may be expected.

Hydrothermal reaction of χ-alumina + boehmite mixture

The products of gibbsite decomposition in air were characterized by thermogravimetry, IR and X-ray diffraction. The major product was the χ-oxide, but a smaller amount of boehmite was also present. In the following, the results of the hydrothermal treatment of χ-alumina + boehmite mixtures are discussed. The samples treated for different periods were analysed by TG, which showed that gibbsite (or some other trihydroxide) was present in the mixture in a certain time interval.

The amount of trihydroxide (as gibbsite) *vs.* the logarithm of time curves are presented in Figs 2-4 for samples processed at 130°. Figures 2 and 3 contain the conversion curves of dry-ground and wet-ground samples, respectively. In order to help the comparison, the curves of two dry and two wet-ground samples are shown in Fig. 4.

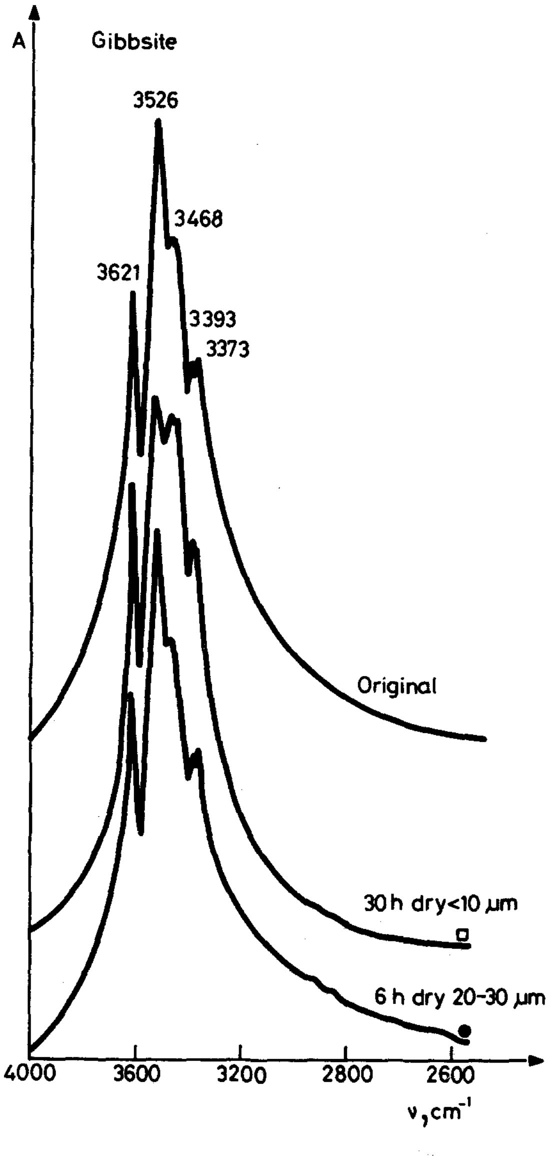


Fig. 1 IR-spectra of gibbsite samples: □ after 30 hours of dry grinding, particle size <10 µm; ● after 6 hours of dry grinding, particle size 20-30 µm

TG and X-ray analysis proved that the final product of hydrothermal treatment was boehmite. The starting boehmite content of the samples probably did not undergo transformation during the treatment.

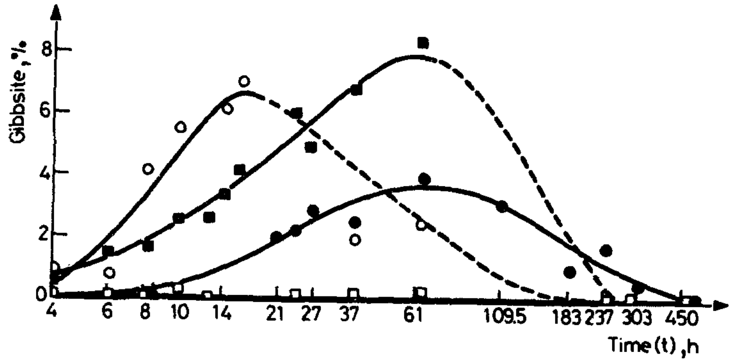


Fig. 2 Hydrothermal treatment of χ-oxide at 130°C. Starting gibbsite: o after 6 hours of dry grinding, particle size 20-30 μm ;■ after 30 hours of dry grinding, particle size 20-30 μm ; □ after 6 hours of dry grinding, particle size <10 μm; • after 30 hours of dry grinding, particle size <10 μm

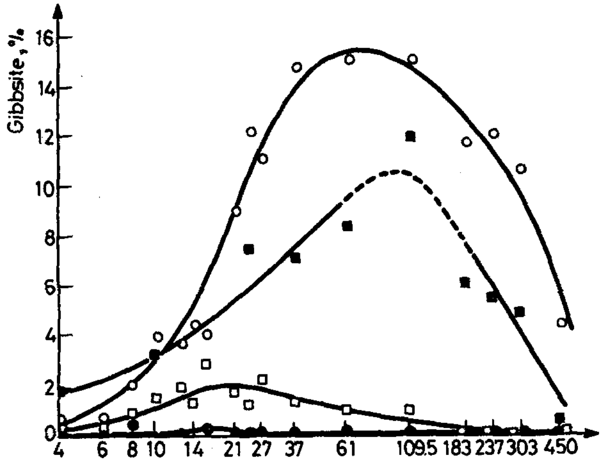


Fig. 3 Hydrothermal treatment of χ-oxide at 130°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size 20-30 μm ; □ after 6 hours of wet grinding, particle size <10 μm; • after 30 hours of wet grinding, particle size <10 μm

The reactions to gibbsite and to boehmite were faster at higher temperatures. More gibbsite was formed at lower temperatures, and the maxima of the gibbsite formation curves were located at longer times.

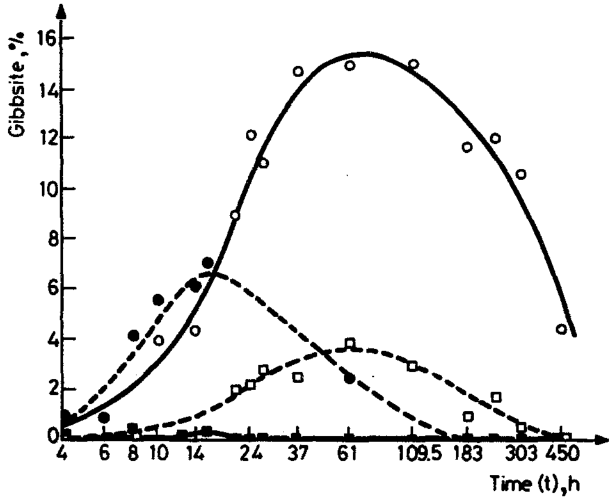


Fig. 4 Hydrothermal treatment of χ-oxide at 130°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size <10 μm; □ after 30 hours of dry grinding, particle size <10 μm

A comparison of Figs 2 and 3 reveals that the transformation of dry-ground samples is usually faster than that of wet-ground ones; and less gibbsite is formed. If samples of the same particle size which have been ground in the same way are compared, the conversion to boehmite is accelerated by longer mechanical treatment. This can probably be explained by the different mechanical activation.

Among the phases occurring in the system, χ-alumina and boehmite were assumed to be the form with the highest free energy and the thermodynamically most stable phase, respectively. Accordingly, the χ-alumina → gibbsite reaction is kinetically favourable at the beginning; later, gibbsite is transformed to the stable boehmite.

Conversion curves of larger particles ground for a shorter time and of smaller particles ground for a longer time are given in Fig. 4. In the former case, the sample previously subjected to a more intensive mechanical activation reacted faster, which corresponds to the above assumptions. However, in the case of samples ground for 30 hours, the opposite was observed: the material obtained from wet-ground gibbsite was transformed more rapidly and a small amount of gibbsite was detected during the process. Further investigations are needed to elucidate this problem.

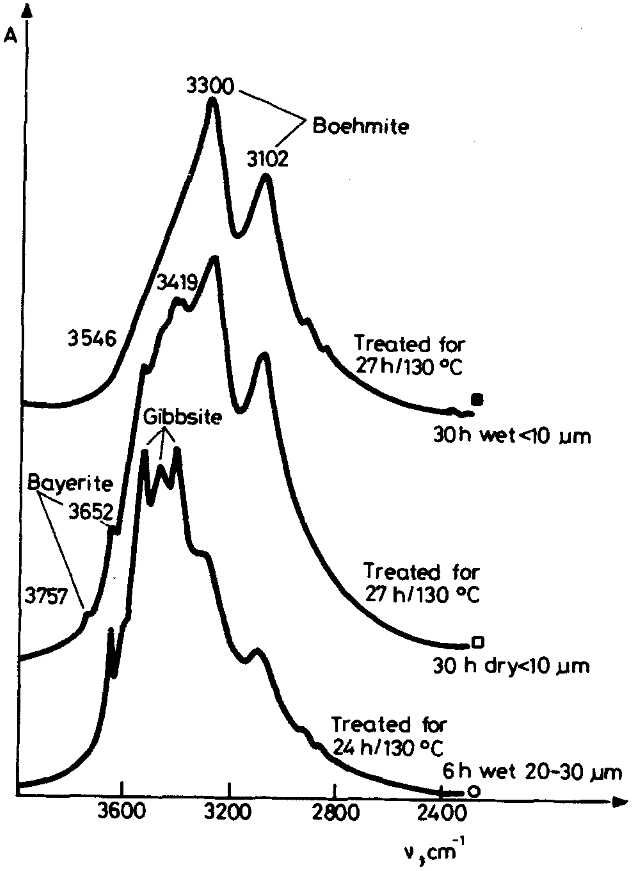


Fig. 5 IR-spectra of hydrothermally treated χ-oxide boehmite mixtures. Starting gibbsite: ■ after 30 hours of wet grinding, particle size <10 µm; □ after 30 hours of dry grinding, particle size <10 µm; o after 6 hours of wet grinding, particle size 20-30 µm

In good agreement with the results of thermoanalytical measurements, the IR spectra in Fig. 5 show that the formation of the boehmitic phase is favoured by a longer mechanical activation and a small particle size. The spectra also show that, among the samples prepared from gibbsites ground for the same time, the material originating from wet-ground gibbsite was practically pure boehmite, while the other two samples contained bayerite and gibbsite as well.

Hydrothermal reaction of gibbsite to boehmite

Conversion curves obtained in three isothermal treatments are demonstrated in Figs 6-8; the IR spectra of the resulting boehmites are given in Fig. 9. In our experience, a 10 deg increase in the temperature of isothermal treatment resulted in a 4-5-fold increase in the rate of transformation. At a given temperature, the duration of the mechanical treatment and the specific surface area both had an acceleratory effect on the rate.

In the case of smaller particle sizes, boehmite was formed faster from the samples subjected to a longer mechanical treatment (dry-grinding). However, this trend was the opposite for larger particles.

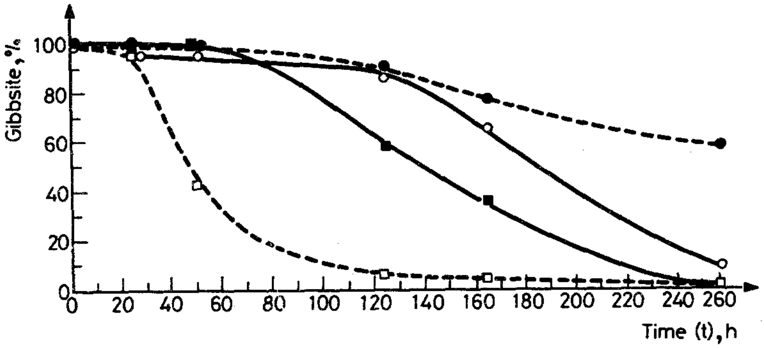


Fig. 6 Hydrothermal conversion of gibbsite to boehmite at 180°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size < 10 μm; □ after 30 hours of dry grinding, particle size < 10 μm

In the IR spectra of hydrothermally formed boehmite (Fig. 9), characteristic bands occurred at 3282 and 3090 cm^{-1}. The intensities of these absorptions were different for samples ground for 30 and 6 hours, pointing to a distortion of the boehmite structure, which may likewise influence the reactivity.

Decomposition of boehmite to γ-alumina

Boehmite samples prepared under identical conditions were decomposed at 490 and 507°. The amount of remaining boehmite is plotted as a function of time in Figs 10-11. Clearly, the small size fraction of the material dry-ground for a longer period reacted most rapidly, while the conversion curves of the other three samples are practically the same.

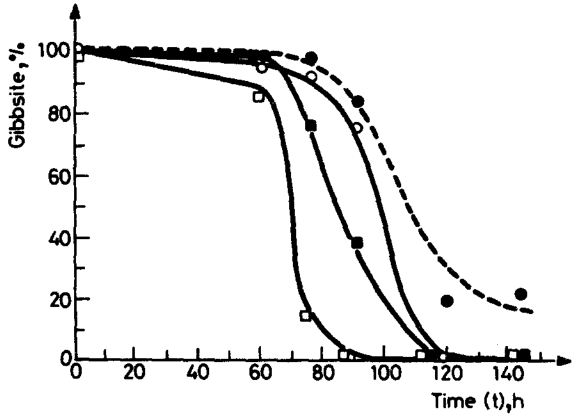


Fig. 7 Hydrothermal conversion of gibbsite to boehmite at 182°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size <10 μm; □ after 30 hours of dry grinding, particle size <10 μm

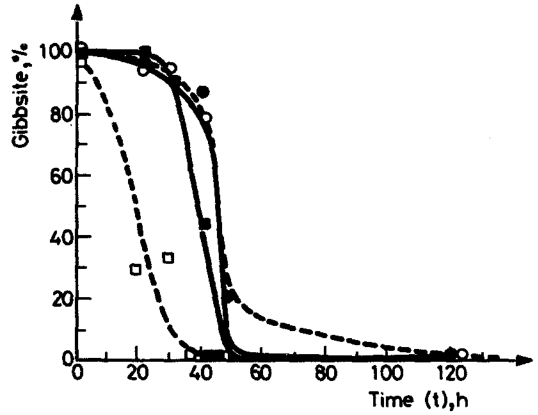


Fig. 8 Hydrothermal conversion of gibbsite to boehmite at 190°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size <10 μm; □ after 30 hours of dry grinding, particle size <10 μm

The IR spectra of γ-aluminas were also informative (Fig. 12). The broad absorption at 840 cm^{-1} is characteristic of the Θ-oxide [17], and the 908 cm^{-1} band in the spectra of samples ground for 30 hours is most probably due to the presence of δ-alumina [17]. This is in agreement with the well-known fact that thermal treatment of boehmite yields several oxide phases.

Hydrothermal reaction of γ-alumina

In the hydrothermal reaction of γ-oxide, boehmite formation was observed. The transformation was facilitated by a higher temperature of isothermal treatment. However, no significant relationship was observed between the different properties of the starting gibbsite and the reactivity of the γ-alumina.

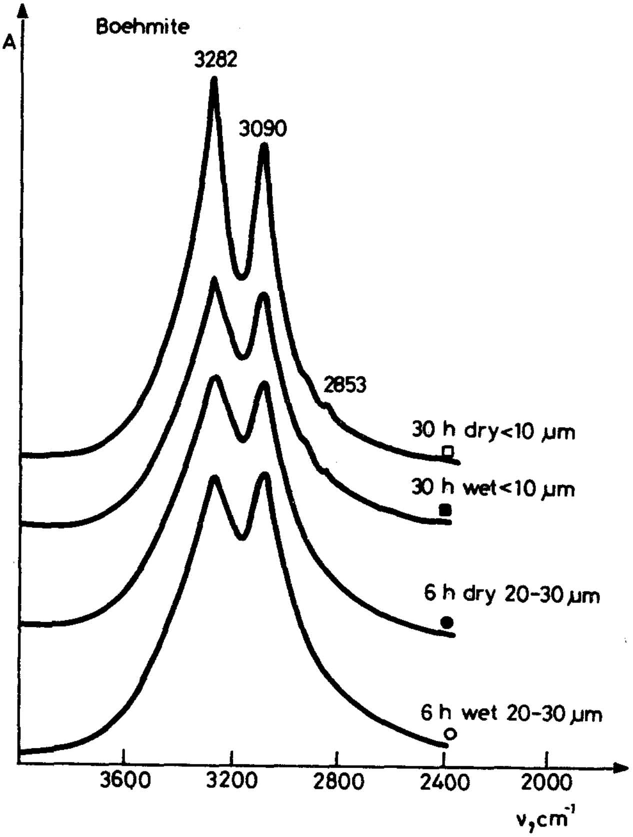


Fig. 9 IR spectra of hydrothermally formed boehmite after treatment for 25 hours at 200°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size < 10 μm; □ after 30 hours of dry grinding, particle size < 10 μm

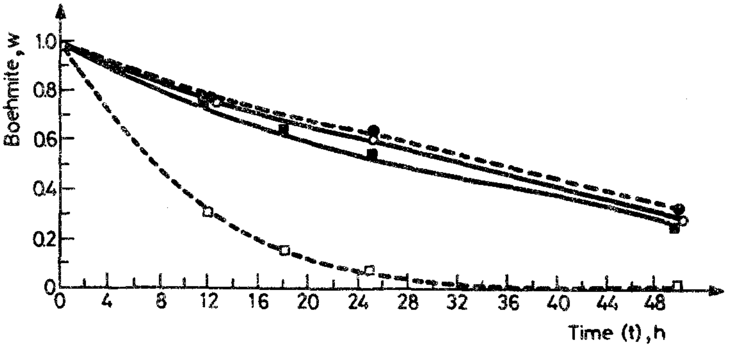


Fig. 10 Decomposition of boehmite to γ-oxide at 490°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μ; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size <10 μm; □ after 30 hours of dry grinding, particle size <10 μm

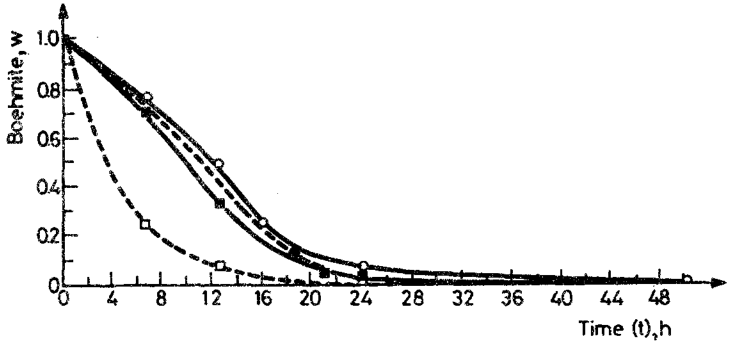


Fig. 11 Decomposition of boehmite to γ-oxide at 507°C. Starting gibbsite: o after 6 hours of wet grinding, particle size 20-30 μm; • after 6 hours of dry grinding, particle size 20-30 μm; ■ after 30 hours of wet grinding, particle size <10 μm; □ after 30 hours of dry grinding, particle size <10 μm

A comparison of the IR spectra of boehmites prepared hydrothermally from gibbsite and boehmites formed in the rehydration of γ-alumina revealed that the latter had a distorted structure (Figs 9 and 13).

Both γ-Al_2O_3 samples were kept at 210° for 10 hours under hydrothermal conditions. The spectrum of the small size fraction of the material ground for a longer time contained a shoulder at about 3500 cm^{-1}. Therefore, the structure of this boehmite may be regarded as more ordered than that of the boehmite prepared from the starting material with larger particle size which was ground for 6 hours.

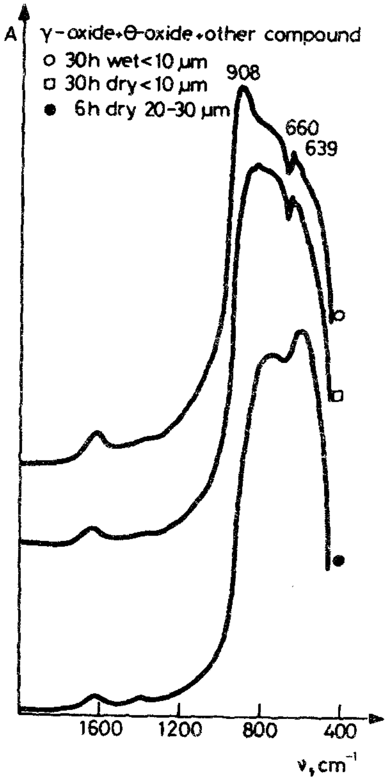


Fig. 12 IR spectra of decomposed boehmite samples, treatment in air at 24 hours at 530°C. Starting gibbsite: • after 6 hours of dry grinding, particle size 20-30 μm; o after 30 hours of wet grinding, particle size < 10 μm; □ after 30 hours of dry grinding, particle size < 10 μm

Conclusions

The method and duration of grinding of the starting gibbsite have marked effects on the reactivity of the gibbsite itself and the primary decomposition products (χ-alumina and boehmite). In the case of these substances, the samples subjected to a greater mechanical activation reacted faster. In a later step of the reaction sequence (hydrothermal treatment of γ-alumina), the differences were insignificant.

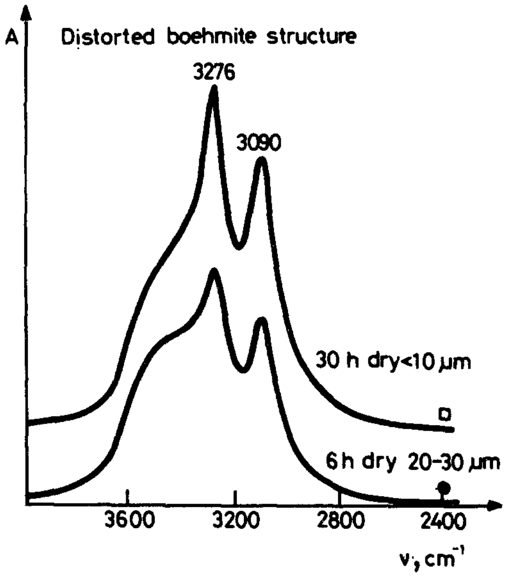


Fig. 13 IR spectra of hydrothermally treated γ-oxide samples. Starting gibbsite: • after 6 hours of dry grinding, particle size 20-30 μm (treated for 10 hours at 210°C) ; □ after 30 hours of dry grinding, particle size < 10 μm (treated for 10 hours at 210°C)

The hydrothermal reactions of gibbsite, those of the χ-alumina + boehmite mixtures and the decomposition of boehmite were faster in the case of the smaller particle size fractions. Accordingly, these reactions may be regarded as basically surface processes.

The final product of the rehydration reactions in the range 120-210° is boehmite, confirming the suggestion of the thermodynamic stability of boehmite in this region [2]. Our experiments also confirmed that, of the hypothetical reaction schemes summarized in Ref. 1, path c (i.e. dehydration to χ-alumina as the main product and boehmite) can be accepted in the given range of parameters.

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Zusammenfassung — Es wurden die hydrothermischen und Zersetzungsreaktionen verschiedener Gibbsitproben und deren Reaktionsprodukten untersucht. Die Proben wurden unter hydrothermischen Bedingungen oder in Luft isothermisch behandelt, die Produkte mittels TG und IR beschrieben. Es wurde festgestellt, daß Art und Weise der Zerkleinerung und Korngröße des Gibbsit-Ausgangsmateriales die Reaktivität von Gibbsit selbst, aber auch die der primären Reaktionsprodukte beeinflußt. In späteren Schritten des Reaktionsverlaufes (hydrothermische Rehydratation von-Aluminiumoxid) besitzen Unterschiede in den Eigenschaften des Gibbsit-Ausgangsmateriales keinen Einfluß.