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PREPARATION OF ALUMINAS

The Effect of Heat Treatment on the Properties of Alumina

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Aluminium hydroxide was prepared by precipitation from aluminium nitrate solution with ammonia solution. Thermal decomposition of the solid hydroxide was studied by means of TG, DTG and DTA.

The sample was thermally treated in the temperature interval between 200 °C and 1000 °C. X-ray phase analysis was used to study the phase compositions of the resulting products, and their surface areas were compared.

The study of alumina is of great importance because it is a large volume product on the chemical market. Although the major part of it is used in the production of aluminium metal, an increasing amount is employed in other fields, e.g., ceramics, abrasives, medicaments, adsorbents and catalysts [1].

It is well known that there are two general classes of aluminas the low surface area α-form or corundum, and the highly porous aluminas, which are of catalytic interest. The chemical structure of alumina has been studied in detail [1–3], and a surface model has been described [4]. This model is based on the assumption that a mixture of low-order planes, viz. the [111], [110] and [100] planes of the spinel lattice, are exposed.

The chemical structure of alumina is complicated by the existence of a number of different phases [5–7]. It has been shown that the important variables for catalytic activity, such as the crystal structure, the pore structure and the chemical nature of the surface, are greatly influenced by the method of preparation [1, 8–11]. This is based on the form of the original hydroxide and the temperature of its denydration [1]. With increasing temperature, a series of forms of Al_2O_3 are produced, with distinct crystal structures, before the α-form, corundum is reached. These intermediates are described by the prefixes γ (gamma), η (eta), χ (chi), δ (delta), θ (theta) and $\varkappa$ (kappa) [11].

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The aim of this research work is to understand the mechanism of dehydration of the hydroxide and to identify a number of crystalline forms of alumina using X-ray, thermal (TG, DTA and DTA) and surface area measurement techniques. Moreover, the structural properties of the prepared alumina are compared with those of commercial alumina samples used as catalysts supports.

Experimental

Materials

Aluminium hydroxide was prepared by slowly adding an aqueous solution of 1 *N* aluminium nitrate to a solution of 1 *N* ammonium hydroxide with constant stirring. The precipitate formed was filtered off, washed with distilled water and dried at 120° for 50 hours. It was treated thermally in temperature intervals between 200° and 1000° for 24 hours. Three samples of commercial alumina (2–4 mm spheres) used as catalyst supports, from different industrial companies,. were used in this work.

Techniques

TG and DTG were carried out with a Stanton 760 thermal analyzer. The rate of heating was 25 deg $\cdot$ min^{-1} in the range 20–1100°. DTA was performed with a Hereaus TA 500 thermal analyzer at a heating rate of 10 deg $\cdot$ min^{-1}.

X-ray measurements were made with a Phillips 1380/00 diffractometer with Cu K_α radiation obtained through a Ni filter. The X-rays were detected with a Xe-proportional counter at a scanning speed of 2° in 20 per minute. All X-ray samples were prepared and measured under the same conditions and the data were compared with those of the ASTM cards.

Surface area measurements were made by the standard BET method with a Carlo–Erba sorptometer apparatus. Before each determination, the sample was evacuated at 250° for 4 hours. Nitrogen was used as the adsorbate at the temperature of liquid nitrogen.

Results and discussion

TG, DTG and DTA

Figure 1 presents the TG, DTG and DTA curves of the hydroxide and the transformation to aluminium oxide. The TG curve showed that the weight loss at 100° was about 4%. This might be due to the loss of the water of hydration [1, 11].

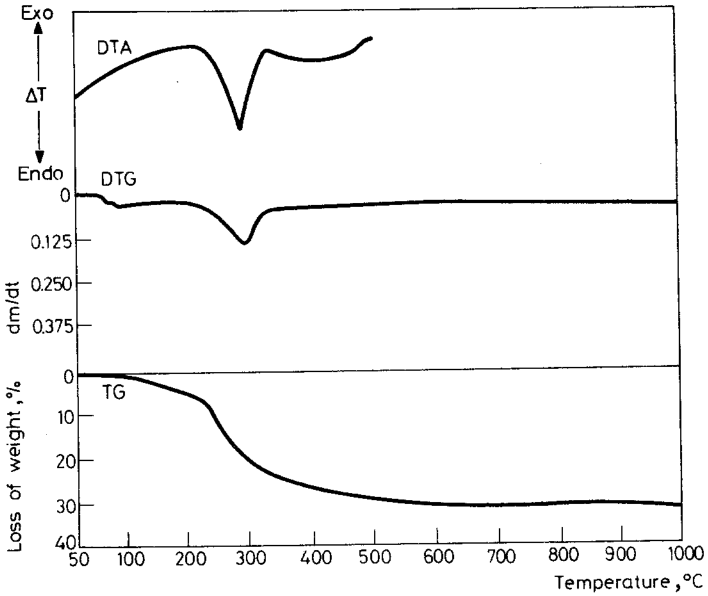

Fig. 1 TG, DTG and DTA curves of the decomposition of the aluminium hydroxide

A strong endothermic peak with maximum at 280° was observed in the DTA and DTG curves. The weight loss calculated from the TG curve at this temperature was found to be 30.78%. This peak may correspond to dehydroxylation of the hydrated alumina [12, 13]. After this temperature, no other weight loss was observed.

X-ray investigations

The X-ray diffraction pattern of the original product heated at 200° indicated well-crystallized bayerite [β-Al(OH)], with a lower amount of gibbsite [α-Al(OH)], as shown in Fig. 2.

The splitting in the [001] reflection of bayerite at 4.86 Å is an effective guide for distinguishing bayerite from gibbsite (ASTM; 15–136, 7–324).

X-ray diffraction patterns of the prepared aluminium hydroxide heated in the temperature interval between 200° and 1000° are shown in Fig. 3. Table 1 details the effects of heat treatment on the phase composition of the resulting alumina.

The X-ray pattern of the original hydroxide heated at 300° indicated poorly-crystallized γ and probably η-alumina (ASTM, 10–425 and 4–875), though it is difficult to distinguish between the two forms [14]. The broad and diffuse peaks at 3.13 Å and 6.11 Å and the splitting in the [440] reflection are indications of the presence of boehmite [γ-AlO(OH)] (ASTM, 21–1307).

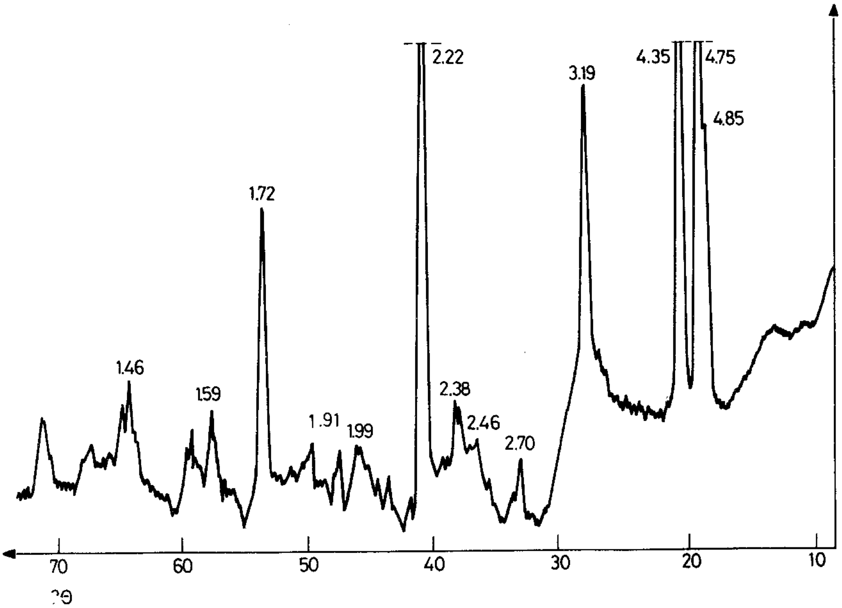

Fig. 2 X-ray diffraction pattern of the prepared aluminium hydroxide

Table 1 The crystal phases and surface area measurements of the resulting oxides after heat treatment of the prepared aluminium hydroxide

Temperature, °C	Oxide form	Specific surface area, $m^2 \cdot g^{-1}$
200	β-Al(OH)$_3$ & α-Al(OH)$_3$	310
300	γ-Al$_2$O$_3$ — γ-AlO(OH)	289
400	Poorly crystallized η & χ-phases	269
500	γ-phase	173
600	γ & trace of the δ-phase	153.5
700	γ & δ-phases	148.5
800	Poorly crystallized θ-phase	117.8
900	Well-ordered θ-phase	84.5
1000	Well-ordered θ-phase	50.3
Commercial (a)	γ & trace of the δ-phases	197
Commercial (b)	γ & δ-phases	155
Commercial (c)	γ & δ-phases	150

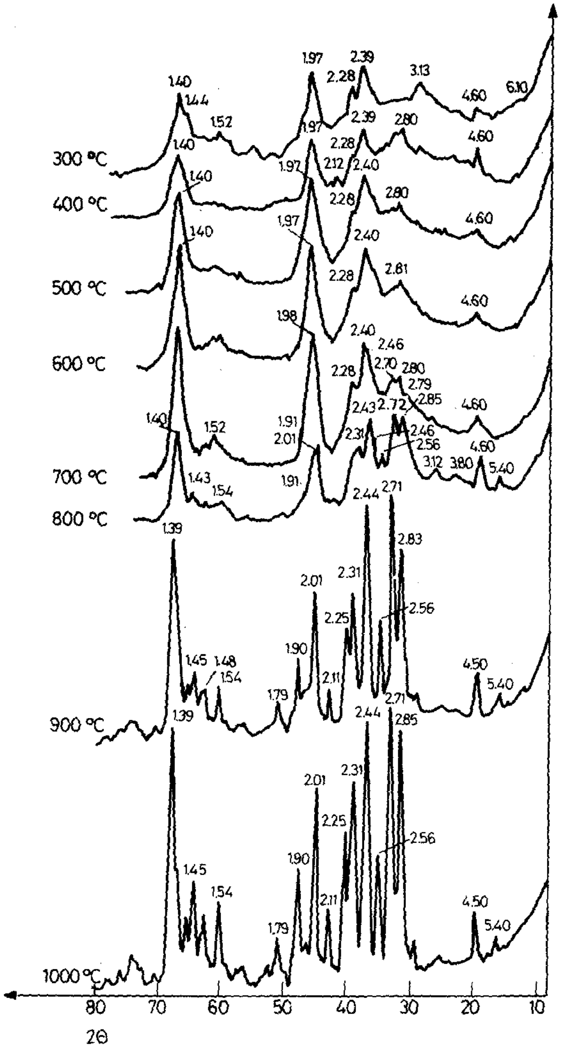

Fig. 3 X-ray diffraction patterns of the aluminium hydroxide heated for 24 hr at temperature indicated

Amorphous boehmite is also a possibility. This transformation is consistent with the thermal analysis results. At 400°, the X-ray pattern is very similar, except for the disappearance of the boehmite peaks. The appearance of the diffuse reflection at 2.12 Å might be due to the formation of a low amount of the χ-phase. The other reflections are practically coincident with the γ-phase reflections (ASTM, 4–0880).

Upon calcination at 500°, well-ordered γ-phase is formed, as the [400] and [440] reflections at 1.977 Å and 1.39 Å are clearly observed. At 600° they become more

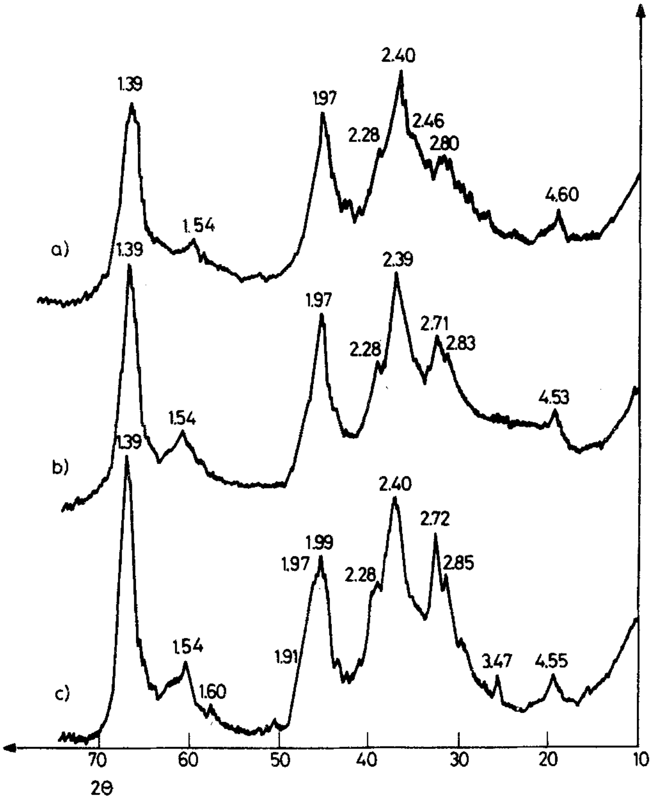

Fig. 4 X-ray diffraction patterns of the commercial aluminas

intense and sharp. The splitting of the [400] reflection at 1.97 Å and 1.95 Å and the appearance of the reflection at 2.71 Å might be due to formation of the δ-phase (ASTM 16–394).

This is more clearly observed upon heating at 700°. The reduced broadening of the lines might be due to the increased crystal growth upon heating. With increasing temperature to 800°, a new structure transition appears, representing the θ-phase (ASTM 11–517). A shift in the [400] reflection from 1.98 Å to 2.01 Å, and splitting at 1.91 Å, are clearly observed. Moreover, the appearance of the new lines of spacing at 2.31 Å and 2.25 Å and the relatively low-order line at 5.4 Å distinguishes the θ-phase from all the other transition structures [1]. Upon final calcination at 900° and 1000°, an X-ray pattern with sharp and intense peaks was produced, with interplanar spacings characteristic of θ-Al_2O_3.

The X-ray diffraction patterns of the three alumina samples (a), (b) and (c), commercially used as catalyst supports, are shown in Fig. 4.

It can be seen that the γ-phase is the major constituent in the three samples. A small amount of the δ-phase is present in sample (b), and it is more clearly observed in sample (c). As compared with the phase composition of the prepared alumina, it is concluded that the commercial samples were heated at temperatures between 500° and 700°. Moreover, from the appearance of the δ-phase and the slightly reduced broadening of the X-ray diffraction lines for samples (b) and (c), it is concluded that they were heated to temperatures near 700°.

It is worth mentioning that a sharp distinction between different types of alumina is more complicated when one is dealing with mixtures. Moreover, the broadening of the lines due to poorly-crystallized aluminas makes identification of the X-ray lines rather difficult.

Surface area measurements

The surface areas of the thermal products were measured. The effects of temperature on the specific surface area are listed in Table 1.

The aluminium hydroxide was initially produced in particles so tiny that had an appreciable surface area on their external geometry [15]. As the hydroxide is heated, water is driven off and it transforms first to a monohydrate and then to a succession of nearly anhydrous crystalline forms. As heating is continued above 400°, crystal growth sets in, so that the surface area diminishes, which is in agreement with the findings of Janiak [16].

The surface areas of the commercial aluminas are also listed in Table 1. It can be observed that catalyst (a) has the highest surface area, and that of catalyst (b) is slightly higher than that of catalyst (c).

As with the X-ray results, the surface areas of the commercial alumina samples (b) and (c) are approximately the same as that of the prepared alumina sample when heated in the range 600–700°.

Conclusion

All the crystallographic structures of the aluminas are based on a more or less cubic close-packed oxygen lattice, with Al-ions in the octahedral and tetrahedral interstices. The various transitions comprise stages in the redistribution of Al-atoms in the tetrahedral or octahedral holes [4]. This cation displacement in the lattice is the most important mechanism for the formation of the different forms of alumina. Above 1000°, a more drastic change, in which the oxygen ion arrangement switches from cubic to hexagonal close-packing, leads to the formation of the α-form [1]. At temperatures between 200° and 300°, the hydroxides are transformed to the appropriate oxides with a loss of water of hydration. This is obvious from the large endothermic peak near 280° and the drop in the surface area. Above this temperature, no other change is observed in the TG curve. Heat treatment above this temperature may effect some crystal growth with deformation of the cubic spinel lattice. This is disclosed by the X-ray powder pattern of new oxide phases and the gradual decrease in the surface area.

γ-Alumina is reported to be used as a catalyst support in different industrial processes. Most of the commercial aluminas used as catalyst supports in fact consist of γ-alumina and a considerable amount of other phases [17]. In our case, it is concluded that the γ-phase is formed at temperatures between 500° and 700°. This is confirmed by comparison with the commercial aluminas used as catalyst supports. The surface area results in this range are also consistent with our results.

Finally, it is concluded that the optimum temperature of dehydration in order to obtain the γ-phase is between 500 and 700°. At temperatures near 700°, our results are consistent with those on the commercial samples as concerns their crystal structures and surface areas.

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Zusammenfassung — Aus einer Aluminiumnitratlösung wurde mit Ammoniaklösung durch Präzipitation Aluminiumhydroxid gefertigt. Mittels TG, DTA und DTG wurde die thermische Zersetzung des festen Hydroxides untersucht. Die Probe wurde Temperaturen zwischen 200 °C und 1000 °C ausgesetzt. Die Phasenzusammensetzung der erhaltenen Produkte wurde mittels Röntgenphasenanalyse untersucht und die Oberflächenstrukturen verglichen.

Резюме — Методами ТГ, ДТГ и ДТА изучено термическое разложение осажденной гидроокиси алюминия, полученной из растворов нитрата алюминия и аммиака. Образец термически обрабатывался в температурном интервале 200–1000°. Фазовый состав образующихся при этом продуктов был изучен с помощью рентгенофазового анализа и сопоставлена их удельная площадь поверхности.