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Sintering of pseudo-boehmite and γ-Al_2O_3

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Sintering of pseudo-boehmite, acicular γ-Al_2O_3 produced by dehydration of pseudo-boehmite, and γ-Al_2O_3 ex alum was investigated. The sintering process was studied by X-ray diffraction, transmission electron microscopy with selected area electron diffraction and BET surface area measurements. The solid state reaction to α-Al_2O_3 causes a steep drop of the surface area to less than $10\ m^2\,g^{-1}$. The acicular pseudo-boehmite and γ-Al_2O_3 supports exhibit an intermediate state where the acicular particles assume a rod-like shape and the surface area falls from about 300 to $100\ m^2\,g^{-1}$. It was established that reaction to α-Al_2O_3 and, hence, sintering proceeds via a nucleation and growth mechanism. The rate-limiting step is nucleation of α-Al_2O_3. Consequently, the contacts between the elementary alumina particles dominate the sinter process. The contact between the acicular elementary particles of pseudo-boehmite and γ-Al_2O_3 studied leads to the reaction to α-Al_2O_3 to be almost complete after keeping samples for 145 h at 1050 °C. Decomposition of alum produces very small particles showing negligible mutual contacts. Consequently an elevated thermal stability is exhibited. Treatment of the alumina ex alum with water and drying results in a xerogel in which contact between elementary particles is much more intimate. Accordingly, treatment at 1050 °C causes a sharp drop in surface area.

1. Introduction

For many catalysts used in industrial processes, γ-Al_2O_3 is undoubtedly a superior support material. It combines a high surface area with a high thermostability. Especially in reactions where steam is either a diluent or one of the reacting components or products, the thermostability is much better than that of other supports, such as SiO_2, TiO_2 and MgO.

γ-Al_2O_3 is mainly produced by dehydration of bayerite or gibbsite [1, 2]. This results in γ-Al_2O_3 of a high porosity, and surface areas which may be as high as $300\ m^2\,g^{-1}$ [3]. Many publications [4–14] have dealt with the crystallographic structure, porous texture, and transformation of low-temperature transition aluminas to the thermodynamically most stable α-Al_2O_3. Dehydration of pseudo-boehmite to γ-Al_2O_3, and subsequent transition to α-Al_2O_3 can be schematically represented as

$$AlOOH \rightarrow \gamma\text{-}Al_2O_3 \rightarrow \delta\text{-}Al_2O_3$$
$$\rightarrow \theta\text{-}Al_2O_3 \rightarrow \alpha\text{-}Al_2O_3$$

γ-Al_2O_3 has a cation deficient spinel structure, consisting of cubic close-packed oxygen anion layers, with cations occupying octahedral and tetrahedral sites. The anhydrous forms (δ-Al_2O_3 and θ-Al_2O_3) are described as transition phases, since they are both metastable with respect to the α-structure. The cubic close packing of the oxygen ions, which characterizes the spinel-type structure, is approximately maintained in the metastable structures. The various transitions comprise stages in the ordering or redistribution of aluminium ions in the interstices of the cubic close-packed oxygen framework. The eventual transformation to the α-form involves, however, a more drastic change in which the oxygen ion arrangement switches from cubic to hexagonal close packing.

One of the main drawbacks of alumina supports prepared by dehydration of bayerite or gibbsite is that the major part of the pore volume is present within very narrow pores. With the preparation of catalysts, the presence of narrow pores within the support gives rise to several problems. During application of the active precursor, which is generally performed by impregnation of the support with a solution of the precursor, penetration of the solution into the pore system proceeds slowly, thus impeding a homogeneous covering of the surface of the support. Once loaded into a reactor and thermally pretreated, catalysts based upon these supports suffer from diffusion limitation of reactants and products.

Pseudo-boehmite (AlOOH) consisting of tiny needles has a much more favourable structure. The small, acicular elementary particles exhibit a high surface area per gram, which can be easily covered by active precursor species. We have studied a commercial pseudo-boehmite displaying a surface area of $300\ m^2\,g^{-1}$. Dehydration of pseudo-boehmite results in γ-Al_2O_3, the elementary particles of which are still acicular.

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By decomposing ammonium alum we prepared another alumina consisting of very small elementary particles. The elementary particles of this alumina were much more symmetrical, which causes the surface area-to-volume ratio to be thermodynamically more favourable than that of the acicular supports. Assuming another shape does not provide a drop in surface energy.

The aim of this study is to arrive at a better understanding of the sintering process of pseudo-boehmite, and of γ-Al_2O_3 consisting of essentially non-porous small elementary particles and exhibiting a porous structure which is not liable to transport limitations. One of the most important characteristics of these supports is the fact that the total BET surface area is exhibited by the external surface of the elementary particles. Elementary particles themselves are not porous or have pores that are below the detection limit of the nitrogen sorption equipment. During preparation of catalysts, precursors of the active components can therefore easily cover the surface of the support completely. Furthermore, diffusion is less probable to limit the rate of a catalytic reaction, and the selectivity of a catalyst based on these supports may be less affected.

Sintering during thermal treatment was quantitatively assessed by measuring the BET surface area. The BET data were corroborated by electron microscopy, which provided information about the effects of the thermal treatment on the shape and the size of the elementary particles. The contact between elementary particles could also be well established from electron micrographs. Besides the particles shape, selected area electron diffraction showed the local reaction to α-Al_2O_3. Since many catalysts are utilized at high temperatures in the presence of steam, some experiments at high temperatures with steam have also been performed.

2. Experimental procedure

2.1. Materials

Pseudo-boehmite and two types of γ-Al_2O_3 were investigated, namely a commercially available γ-Al_2O_3 produced by dehydration of pseudo-boehmite at 600 °C (Engelhard De Meern B.V., The Netherlands), and γ-Al_2O_3 prepared by decomposition of ammonium alum.

Major impurities of the commercial alumina as determined by the manufacturer are: 0.15 wt % SiO_2, 0.03 wt % Na_2O, 0.04 wt % Fe_2O_3, 0.03 wt % SO_4^{2-}, and 0.1 wt % Cl^-. Pseudo-boehmite (AlOOH, Al 4170) has a BET surface area of 300 $m^2 g^{-1}$ and a pore volume of 0.84 $cm^3 g^{-1}$. It consists of acicular particles with an average length of 80 nm and an average width of 5 nm. γ-Al_2O_3 (Al 4172) prepared by dehydration of pseudo-boehmite at 600 °C has a BET surface area of 265 $m^2 g^{-1}$ and a pore volume of 1.14 $cm^3 g^{-1}$. Due to the topotactic transformation, the acicular structure of pseudo-boehmite is maintained during the dehydration process.

The second alumina used in this study was γ-Al_2O_3 prepared by decomposition of ammonium alum (Merck p.a). The as-prepared alumina has a BET surface area of 160 $m^2 g^{-1}$ and a pore volume of 1.40 $cm^3 g^{-1}$.

2.2. Preparation of γ-Al_2O_3 ex alum

An amount of $NH_4Al(SO_4)_2 \cdot 12\ H_2O$ was placed in a quartz crucible, and loaded into an electrically heated Heraeus furnace. The furnace was heated to 900 °C at a heating rate of 15 °C min^{-1}, and held at this temperature for 4.5 h. After melting the alum at 94 °C, the liquid rose into a foamy mass from which NH_3 was evolved at 300 °C and SO_3 at 800 °C [15, 16]. After 4.5 h at 900 °C no further weight loss was observed. It was thus concluded that the decomposition was complete. Due to the high temperature at which decomposition was performed, the alumina not only consisted of γ-Al_2O_3, but also contained traces of δ-Al_2O_3.

2.3. Sinter experiments

In order to investigate the sintering behaviour of the aluminas, sinter experiments were carried out in an electrically heated furnace in stagnant air. Samples were placed into alumina crucibles, and loaded into the furnace at room temperature. The furnace was heated to 1050 °C at a heating rate of 15 °C min^{-1}. Samples were held at this temperature for periods up to 145 h, and were subsequently cooled down to room temperature. Sinter experiments were also performed at 700 °C. Samples were held at this temperature for several weeks.

To study the thermostability of alumina samples in the presence of water vapour, sinter experiments were also performed in a mixture of steam and air. Samples were placed into quartz crucibles, and heated at 1050 °C in a flow (100 ml min^{-1}) of 10 and 20 vol % of steam in air for 23 h.

2.4. Procedures

BET surface area measurements were carried out after outgassing samples in vacuum at 200 °C overnight. The specific surface area was calculated from the extent of nitrogen sorption at −195 °C at relative pressures from 0.05 to 0.35. For the surface area per nitrogen molecule a value of 0.162 nm^2 was assumed. The measurements were performed with a Carlo Erba Sorptomatic type 1800.

Transmission electron microscopy (TEM) was done within a Philips EM 420 electron microscope operated at 100 kV. TEM samples were ground in an agate mortar, suspended in ethanol, and submerged in an ultrasonic bath for one minute to ensure homogeneity of the suspension. Drops of this suspension were applied to a holey carbon film supported by a copper grid. Selected area electron diffraction (SAED) patterns were taken at the same accelerating voltage. Calibration was done with evaporated gold films.

Powder X-ray diffraction (XRD) was performed with a Guinier camera equipped with a Johansson monochromator (CuK_{α_1} radiation) in combination

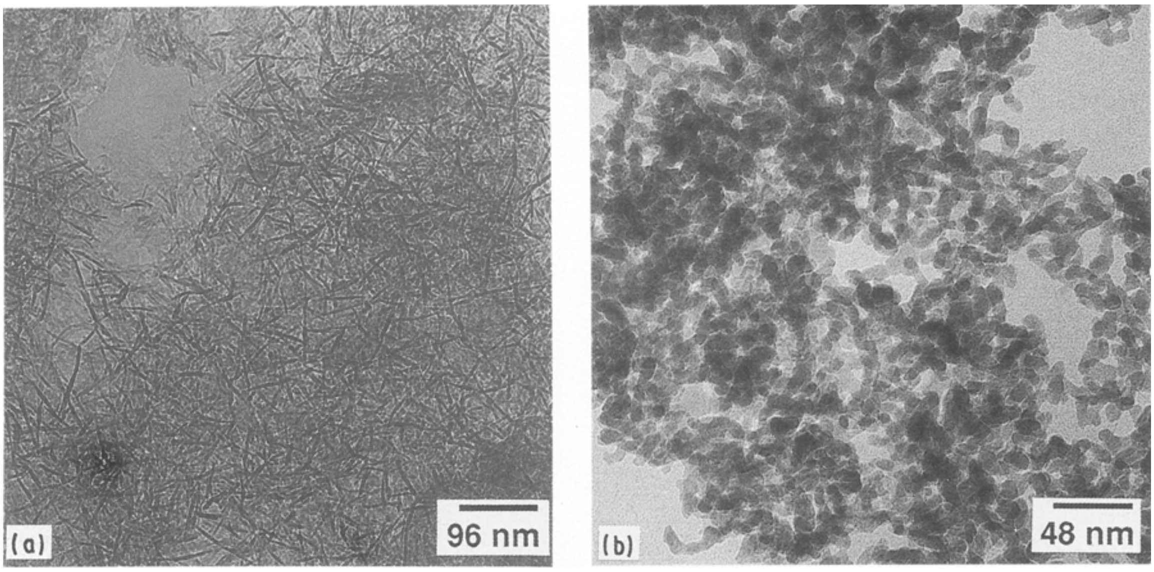

Figure 1 TEM micrographs of (a) γ-Al_2O_3 (Al 4172) and (b) γ-Al_2O_3 ex alum.

with a microdensitometer (Jenoptik MD 100), and a Philips diffractometer PW 1050 ($CuK_{\alpha_{1,2}}$ radiation).

3. Results and discussion

Fig. 1 shows TEM micrographs of the acicular alumina ex pseudo-boehmite and of alumina ex alum.

Surface area against time plots for pseudo-boehmite and the acicular alumina obtained at 1050 °C in stagnant air are presented in Fig. 2. In Fig. 2 it can be seen that the initial decrease in surface area proceeds very rapidly. The surface area of the pseudo-boehmite (Al 4170) had decreased from 300 to 98 $m^2 g^{-1}$ after 6 h at 1050 °C, and the surface area of the γ-Al_2O_3 (Al 4172) from 265 to 98 $m^2 g^{-1}$. In this part of the sintering process, the acicular morphology of pseudo-boehmite and γ-Al_2O_3 (Al 4172) disappeared, and particles of a rodlike appearance resulted. The rods had grown shorter and thicker as compared with the original acicular particles. Assuming a cylindrical shape for the elementary particles, calculated surface areas were in good correspondence with the measured BET surface areas. The similarity between the results obtained for γ-Al_2O_3 and pseudo-boehmite can be explained by the fact that dehydration of pseudo-boehmite to γ-Al_2O_3 proceeds very fast, and took place already during heating the furnace to 1050 °C. XRD patterns show transformation from pseudo-boehmite or γ-Al_2O_3 to θ-Al_2O_3 after 3 h at 1050 °C. This transformation was confirmed by SAED and high resolution TEM.

After the rapid initial decrease in surface area, the subsequent drop proceeds more slowly. This part of the curve corresponds with the transformation of θ-Al_2O_3 to α-Al_2O_3. XRD as well as SAED show the formation of α-Al_2O_3 nuclei growing upon prolonged heating at 1050 °C in a transition alumina matrix. It was observed that initially only clusters of rods oriented in parallel sinter to small platelets of θ-Al_2O_3. On prolonged high temperature treatment, nucleation of the thermodynamically stable α-Al_2O_3 starts within the platelets of θ-Al_2O_3. Recrystallization to α-Al_2O_3 leads to large plates exhibiting a low surface area. Contact between the needles of θ-Al_2O_3 is very important. It was observed that needles barely in mutual contact recrystallize very slowly. A TEM micrograph of a sample of γ-Al_2O_3 (Al 4172) sintered for 145 h at 1050 °C is shown in Fig. 3.

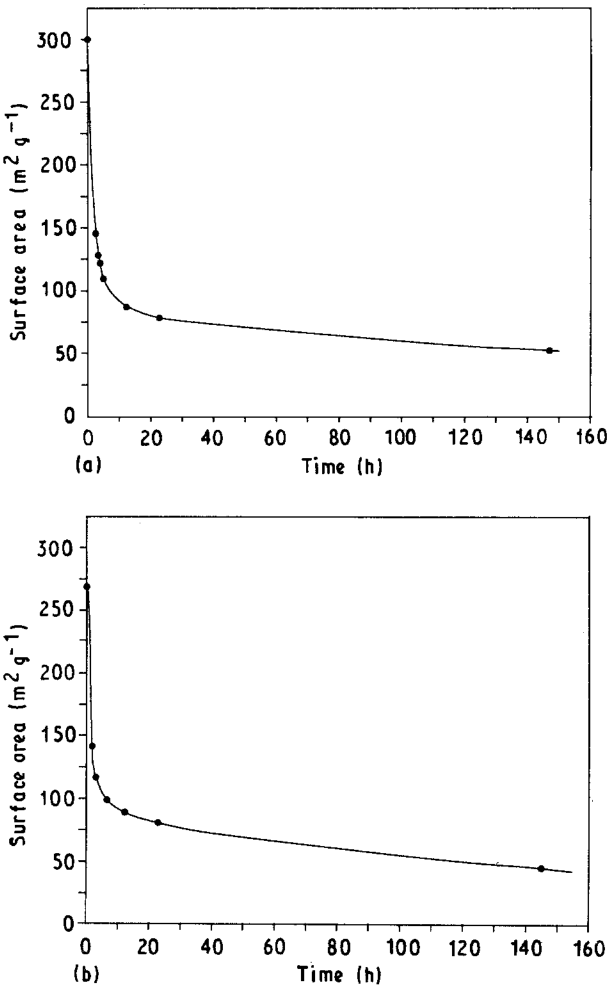

Figure 2 Surface area against time plots obtained at 1050 °C in air for pseudo-boehmite (Al 4170) and γ-Al_2O_3 (Al 4172).

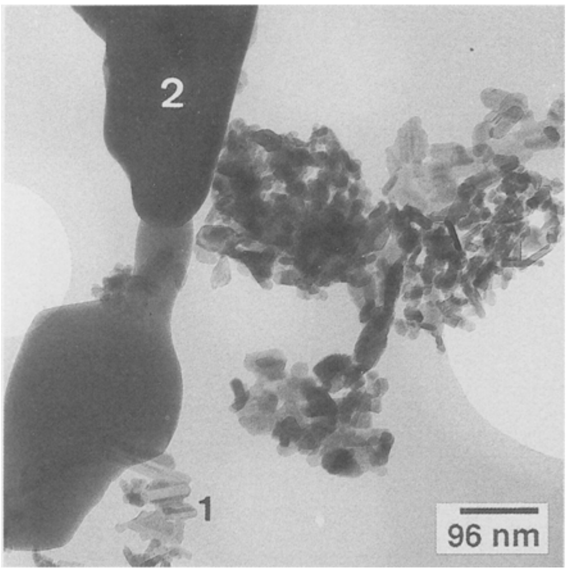

Figure 3 TEM micrograph of γ-Al_2O_3 (Al4172) sintered for 145 h at 1050 °C in air. Note the parallel rods of θ-Al_2O_3 (1) and plates of α-Al_2O_3 (2).

Sinter experiments with γ-Al_2O_3 (Al 4172) were also performed at a temperature of 700 °C. Transformation of γ-Al_2O_3 to θ-Al_2O_3 is not likely at this temperature. The rapid initial decrease in surface area was absent in these experiments. Heating a sample of γ-Al_2O_3 (Al4172) for 250 h at 700 °C resulted in a decrease in surface area from 265 to 185 $m^2\,g^{-1}$. After prolonged heating at 700 °C for 425 h the surface area was 168 $m^2\,g^{-1}$ and the same change in morphology from acicular particles to rods could be observed as in the experiments performed at 1050 °C for 145 h. It can, therefore, be concluded that the decrease in surface area is not caused by the thermodynamically favourable transition from γ-Al_2O_3 to θ-Al_2O_3, but by the decrease in surface area, and thus, in surface energy of the elementary particles.

In Fig. 4 results are presented of the sinter experiments at 1050 °C in air with alumina ex alum. From this figure it can be concluded that γ-Al_2O_3 ex alum did not exhibit the rapid initial decrease in surface area. A remarkable difference between γ-Al_2O_3 ex alum and acicular γ-Al_2O_3 is the very high thermostability of the former. Transformation of γ-Al_2O_3 to θ-Al_2O_3 is facilitated by a large initial surface area, i.e. the rate of sintering is determined by the initial surface area of the alumina [17]. As the initial surface area of alumina ex alum was only 160 $m^2\,g^{-1}$, the limited initial decrease in surface area of the symmetrical elementary particles is obvious.

Sinter experiments have also been performed in 10 vol % of steam in air at 1050 °C. In sinter experiments with pseudo-boehmite and acicular γ-Al_2O_3 (Al4172) no influence of steam could be observed. The results were comparable with those obtained in dry air, resulting in a BET surface area of 85 $m^2\,g^{-1}$ after 23 h at 1050 °C. Raising the steam content to 20 vol % gave the same results.

The alumina ex alum is prepared without the alumina particles being exposed to liquid water and being subsequently dried. The removal of ammonia and sulphur oxide leads to a powder in which the elementary particles are exhibiting hardly any contact.

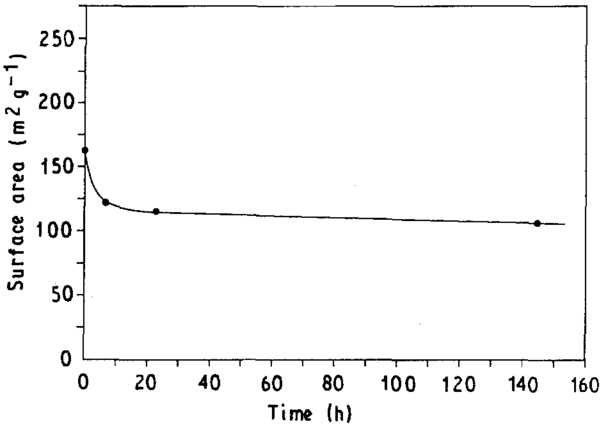

Figure 4 Surface area against time plot obtained at 1050 °C in air for γ-Al_2O_3 ex alum.

Nucleation of α-Al_2O_3 governs the rate of transformation and, hence, the rate of sintering. Without a substantial contact between the elementary alumina particles, nucleation must proceed in almost every elementary particle. Consequently, transformation to α-Al_2O_3 and sintering does not proceed significantly in the alumina produced from alum; the lack of sintering is evident from the modest drop in the BET surface area, namely from 160 to 116 $m^2\,g^{-1}$.

When steam was condensed within the pores of the alumina and the water was subsequently removed by drying, the contact between the elementary particles becomes much more intimate. Due to the surface energy of liquid water, the elementary particles are squeezed together. The improved interparticle contact dramatically decreases the thermostability of the alumina ex alum. Thermal treatment for 24 h at 1050 °C lowered the surface area of the dried powder to 55 $m^2\,g^{-1}$, which is much lower than the surface area of 116 $m^2\,g^{-1}$ exhibited by the powder not being treated with liquid water. Fig. 5 shows a TEM micrograph of γ-Al_2O_3 ex alum being thermally treated at 1050 °C after immersion of water and drying. Formation of large α-Al_2O_3 particles is evident. Provided condensation of steam was prevented, the surface area of γ-Al_2O_3 ex alum was neither more affected by thermal treatment in steam.

The experiments with the alumina ex alum unambiguously demonstrated that transformation to α-Al_2O_3 and sintering is dominated by nucleation of α-Al_2O_3. Growth of the nuclei proceeds more rapidly than nucleation. With small acicular elementary particles, the interparticle contacts are relatively limited. Consequently, transformation of α-Al_2O_3 and sintering proceeds relatively slowly with pseudo-boehmite and γ-Al_2O_3 produced from pseudo-boehmite. Wetting and drying of acicular alumina does not improve the contact between the particles substantially.

It was found that ultrasonic treatment of a dispersion of acicular alumina particles in water leads to formation of clusters in which the alumina needles are

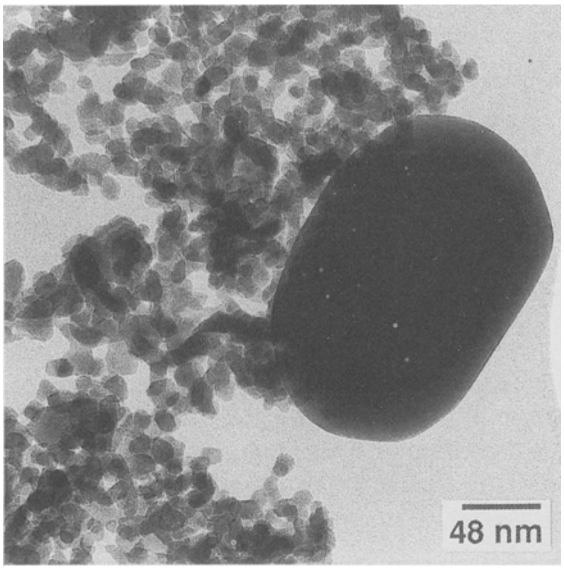

Figure 5 TEM micrograph of a sample of Al_2O_3 ex alum after the steam sinter experiment at 1050 °C for 24 h.

oriented in parallel, exhibiting a close mutual contact. Thermal treatment caused a steep drop in surface area of samples thus pretreated. Electron microscopic investigation showed that formation of α-Al_2O_3 had preferentially occurred within the clusters.

4. Conclusions

In pseudo-boehmite and acicular γ-Al_2O_3 (Al 4172) the elementary particles have a high surface-to-volume ratio. Upon heat treatment, recrystallization from γ-Al_2O_3 to θ-Al_2O_3 proceeds, which, together with a change in shape, leads to a decrease in surface energy. As the surface area-to-volume ratio of the elementary particles of γ-Al_2O_3 ex alum is much smaller, the rapid drop in surface area due to a change in shape does not take place.

Recrystallization from θ-Al_2O_3 to α-Al_2O_3 proceeds upon further heat treatment. Contact between the elementary particles is of paramount importance. The contact between rods of θ-Al_2O_3 is much better than between the small platelets of θ-Al_2O_3 produced from alum. The critical size of a nucleus of α-Al_2O_3 can be reached in samples with an acicular morphology, while this is hardly possible with the alumina ex alum, thus explaining the higher thermostability of the latter sample.

After exposure to liquid water and drying, contact between the symmetrical elementary particles of alumina ex alum is enhanced, and the rate of transformation of θ-Al_2O_3 to α-Al_2O_3 is dramatically increased. Aluminas having needles as elementary particles exhibit a limited interparticle contact and, thus, a relatively high thermal stability.

Since nucleation of α-Al_2O_3 is the rate-determining step, the final surface area of α-Al_2O_3 also strongly depends on the contact between the elementary particles of the transition alumina from which α-Al_2O_3 is to be produced. With a powdered starting alumina, the growth of α-Al_2O_3 grains is limited. A pelletized transition alumina, in which the elementary particles have been pressed together, shows a higher drop in surface area after sintering. The intimate contact between the elementary particles of starting material allow nuclei of α-Al_2O_3 to grow to very large crystallites displaying a low surface area. The surface area resulting from extrudates of a transition alumina is in between the values for powders and pellets.

References

1. B. C. LIPPENS and J. H. DE BOER, *Acta Crystallogr.* **17** (1964) 1312.
2. B. C. LIPPENS, J. J. STEGGERDA, in "Physical and Chemical Aspects of Adsorbents and Catalysts" (Academic, New York, 1970), p. 171.
3. S. SOLED, *J. Catal.*, **81** (1983) 252.
4. H. SCHAPER and L. L. VAN REIJEN, *Thermochimica Acta* **77** (1984) 383.
5. H. SCHAPER, E. B. M. DOESBURG, P. H. M. DE KORTE and L. L. VAN REIJEN, *Solid State Ionics*, **16** (1985) 261.
6. D. S. TUCKER, *J. Amer Ceram. Soc.* **68** (1985) C163.
7. S. J. WILSON, *Mineral. Mag.* **43** (1979) 301.
8. J. F. BERAR, D. GREBILLE, P. GREGOIRE and D. WEIGEL, *J. Phys. Chem. Solids* **45** (1984) 147.
9. D. S. MACIVER, H. H. TOBIN and R. T. BARTH, *J. Catal.* **2** (1963) 485.
10. S. J. WILSON, J. D. C. McCONNELL and M. H. STACEY, *J. Mater Sci.* **15** (1980) 3081.
11. K. J. MORRISSEY, K. K. CZANDERNA, C. B. CARTER and R. P. MERRILL, *Comm. Amer. Ceram. Soc.*, May (1984) C88.
12. M. KUMAGAI and G. L. MESSING, *J. Amer. Ceram. Soc.* **68** (1985) 500.
13. V. A. DZIS'KO, T. S. VINNIKOVA, L. M. KEFELI and I. A. RYZHAK, *Kin. Kat.* **7** (1966) 859.
14. R. S. ALWITT, in 'Oxides and Oxide Films", Vol. IV, 1976, (Marcel Dekker, New York, 1976) p. 169.
15. F. W. DYNYS and J. W. HALLORAN, *J. Amer. Soc.*, **65** (1982) 442.
16. D. W. JOHNSON and P. K. GALLAGHER, *ibid.* **54** (1971) 461.
17. P. BURTIN, J. P. BRUNELLE, M. PIJOLAT and M. SOUSTELLE, *Appl. Catal.* **34** (1987) 225.

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