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CHARACTERISATION OF A FINE ALUMINA POWDER OBTAINED BY THE THERMAL DECOMPOSITION UNDER THE NITROGEN ATMOSPHERE OF THE PRECURSOR WHICH WAS PREPARED BY THE EMULSION EVAPORATION TECHNIQUE

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ABSTRACT

Thermogravimetric (TG) curve of the dark brown precursor which was prepared by the emulsion evaporation technique, was obtained under the nitrogen atmosphere. The thermal decomposition of the precursor which was completed in four steps, was investigated by the Coats- Redfern procedure by using the TG data. Fine alumina powder was obtained from the precursor which was calcined at 1000 °C for two hours, after burning its organic fractions. The particle size distribution (PSD) of the powder was determined and its photographs were taken by an electron microscope. It was determined that the particles, whose sizes were between 0.8-30.0 μm, were composed of inagglomerated spheres, the insides of which were porous.

INTRODUCTION

The first and most important step in the production of high technology ceramics such as, heterogeneous catalyst beds, electronic substrates, nuclear fuels, artificial tissues, abrasives, cutters, magnets, filters, electrical insulators, semi conductors and super conductors is the production of fine ceramic powders [1]. These powders are produced from pure chemical reagents. The intermediate product obtained during the production is called the precursor [2]. Fine ceramic powders are obtained by the calcination of the precursor at 1000 °C for a certain period [3]. During the forming by either of the suspension, casting or pressing procedures, it is required that the particles should have closest packing. Therefore it is necessary that the particles should be equally sized, spherical and as small as possible [4]. High technology ceramics are obtained by sintering of the formed materials at temperatures above 1000 °C for a certain period [5,6].

One of the procedures for the preparation of fine ceramic powders is the emulsion evaporation technique [7-10]. The first aim of this study was the investigation of the thermal decomposition of the alumina precursor which was obtained by emulsion evaporation, under the nitrogen atmosphere. The second aim was the determination of the sizes and shapes of the particles in the powder which was obtained from the calcination of this precursor.

MATERIALS AND METHOD

The optimum conditions for the preparation of an infinitely stable water in oil emulsion was determined in our previous studies [11,12]. According to these conditions, 65 % white mineral oil (AMOCO, 21 USP), 30 % 1.75 M Al $(NO_3)_3$ solution and 5 % Arlacel 83 (ICI Americas) emulgator (represented in volume percents) were mixed. The heterogeneous mixture was stirred by a magnetic stirrer for 30 min and thus an infinitely stable emulsion was prepared. The prepared emulsion was evaporated by dropping it into mineral oil whose temperature was 240 °C. The dark brown precursor which was formed, was separated by centrifugation by a Beckmann TJ-6 instrument for 30 min at a rate of 2500 min^{-1}. The precursor was washed with toluene and dried for 24 hours at 240 °C.

The Thermogravimetric (TG) curve of the precursor was determined by a Dupont 1090 instrument at a heating rate of 5 K min^{-1}, under the nitrogen atmosphere. α-Al_2O_3 was used as an inert material. The particle size distribution of the fine alumina powder which was obtained by the calcination of the precursor at 1000 °C, for four hours, under an atmosphere of air, was determined by a light scattering particle size analyser (Leeds and Northrop, Microtrac SPA). The photograph of the same powder was taken by an electron microscope (JOEL, JSM U-3).

RESULTS AND DISCUSSION

The Thermal Decomposition of the Alumina Precursor under the Nitrogen Atmosphere

The TG curve of the alumina precursor which was obtained by emulsion evaporation at 50-800 °C, under the nitrogen atmosphere, is given in Figure 1.

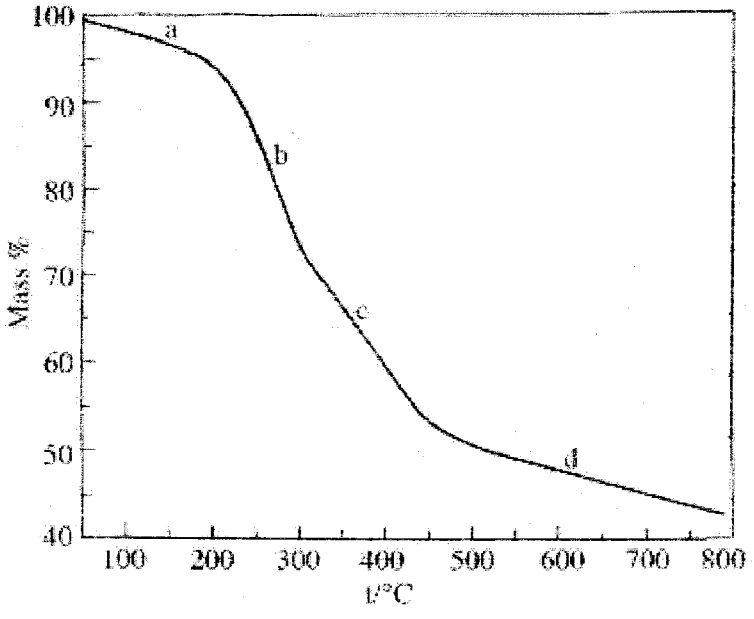

Figure 1. The four stepped thermogravimetric curve of the decomposition under the nitrogen atmosphere of the alumina precursor which was obtained by the evaporation of the emulsion which was prepared under the optimum conditions by using 1.75 M $Al(NO_3)_3$ solution.

It can be observed from this curve that, as the temperature increases from 50 to 800 °C the mass decrease resulting from the elimination of materials by decomposition, is around 57 %. The same decomposition is completed at 550 °C under an atmosphere of air. A closer look at the curve reveals that the thermal decomposition proceeds via four principle steps shown by a, b, c and d. A decomposition factor is defined as the ratio of the total mass decrease at the end of each increase of 25 K in temperature to the total mass decrease which is assumed to stay constant at 800 °C. The variation of the decomposition factor as a function of temperature is given in Figure 2.

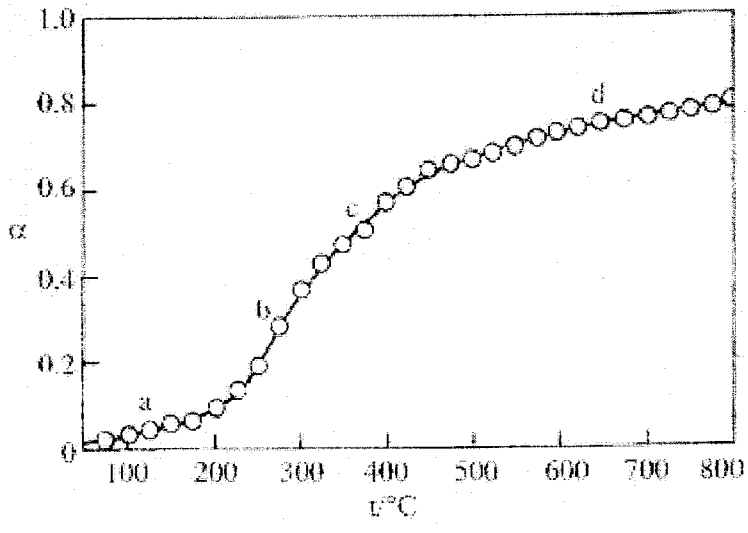

Figure 2. The four stepped curve which shows the variation of the thermal decomposition factor (α) as a function of temperature (t).

For the a, b, c, and d steps, the straight lines were plotted according to the following Coats-Redfern equation

$$\ln \{ [-\ln (1 - \alpha)] / T^2 \} = - (E / RT) + \ln [(AR / \beta E) (1 - 2RT / E)] \qquad (1)$$

where A and E are the Arrhenius constants, E being the activation energy of the decomposition and A being the preexponential factor, T is the absolute temperature, $\beta \equiv dT / dt$ is the heating rate and R is the universal gas constant. These straight lines are given in Figure 3.

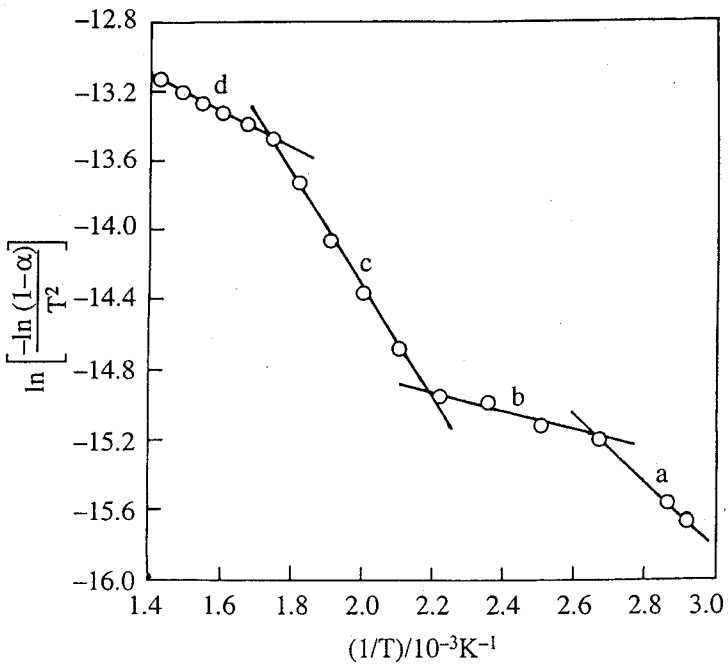

Figure 3. The Coats-Redfern straight lines of the thermal decomposition of the alumina precursor at different temperature intervals.

For the a, b, c and d decompositions the activation energies were calculated from the slopes of straight lines given in Figure 3 and they were, respectively, 16, 4, 27 and 9 kJ mol $^{-1}$. In the interval between 50-200 °C (step a), where the activation energy is relatively small, the most probable decomposition is the elimination of water and toluene in the precursor, by evaporation. In the interval between 200-300 °C (step b), where the activation energy is very small, the most probable decomposition is the evaporation of the organic substances having smaller molecules, which were formed by the partial decomposition of white mineral oil and Arlacel 83, during the formation of the precursor. In the interval between 300-550 °C (step c), where the activation energy is biggest, it can be stated that, a complete thermal decomposition of white mineral oil and Arlacel 83 occurs. Furthermore, the dehydroxylation of raw alumina in the precursor, takes place in this step. In the interval between 550-800 °C (step d), where the activation energy is small, the most probable decomposition is the evaporation of the organic substances having very large molecules, which were formed by the thermal decomposition of white mineral oil and Arlacel 83, during the formation of the precursor.

CHARACTERISATION OF THE PARTICLES

In our previous studies, it was determined by X-ray diffraction that the precursor contained diaspore (β-AlOOH) particles, as raw alumina phase [3]. Among the raw alumina phases called gibbsite, boehmite, bayerite and diaspore only the diaspore can be directly transformed into α-Al_2O_3 at 550 °C [6]. The particle size distribution (PSD) of the fine α-Al_2O_3 powder which was obtained by the calcination of the precursor at 1000 °C, for four hours, is given in Figure 4. In this Figure, it can be observed that the particle size varies between 0.8-30.0 μm and the average particle size is 7.5 μm.

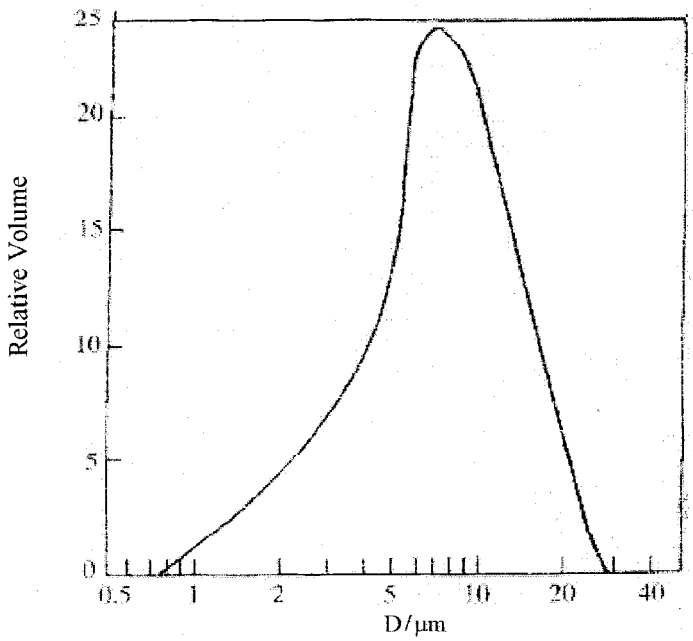

Figure 4. The particle size distribution of the fine alumina powder obtained by the calcination at 1000 °C, for two hours, of the alumina precursor whose organic constituents had been burnt.

The photographs (taken by an electron microscope) of the fine alumina powder, having different magnification are, respectively, given in Figures 5, 6 and 7. In Figure 5 , it is observed that the particles are mostly spherical but have different sizes. Moreover, some of the spheres are agglomerated in couples and some are decomposed. In Figure 6, the splitting of the spheres as a result of bursting is observed. In Figure 7, it is observed that the burst particles are hollow. According to

these determinations, it was decided that the particles were in the form of spherical shells.

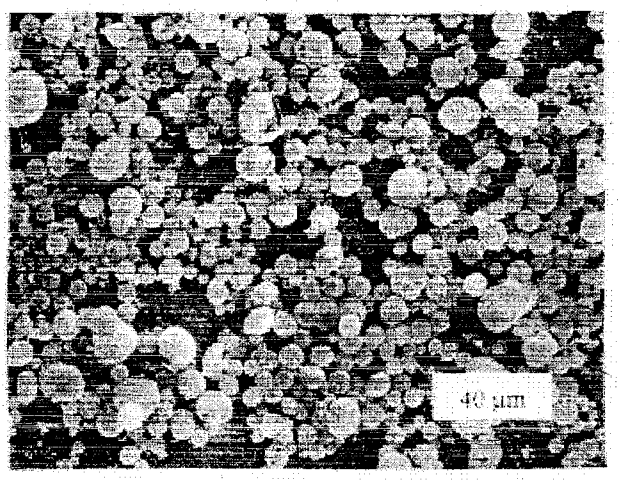

Figure 5. The photograph (taken by an electron microscope) of the fine alumina powder which was calcined.

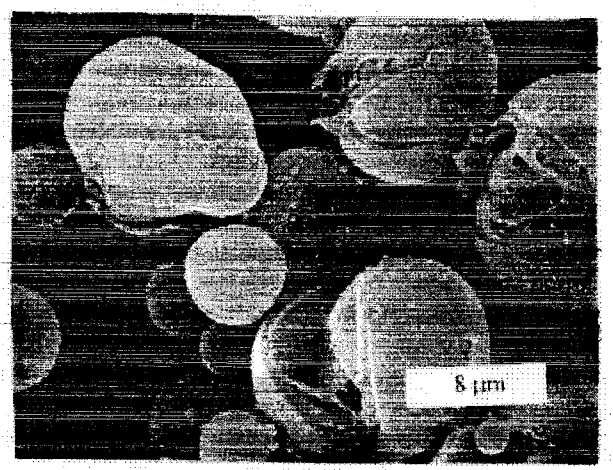

Figure 6. The view through an electron microscope of the spherical, nonspherical

and burst alumina particles, during the emulsion evaporation.

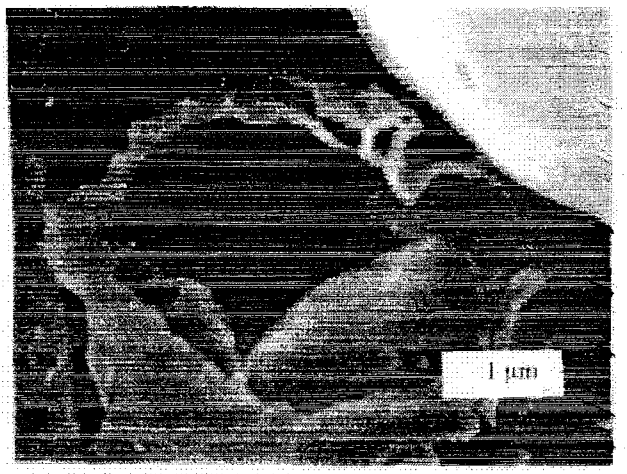

Figure 7. The macroporous view of an alumina particle, during the emulsion evaporation.

CONCLUSIONS

It was observed that, the decomposition of the precursor which was obtained by emulsion evaporation and which contained diaspore as raw alumina, was completed around 800 °C. In our previous studies, it was determined that the thermal decomposition of the same precursor,under an atmosphere of air was completed around 550 °C [3]. The completion of the thermal decomposition under an atmosphere of air at a lower temperature was related to the combustion of organic substances present in the precursor, at around 300-500 °C. It was decided that the fine alumina powder, whose particle sizes varied between 0.8-30.0 μm and which was composed of spherical shells instead of full spheres could be used as catalyst beds, support material for chromatographic columns, filters, membranes and metal polishers. It seems impossible to produce structural ceramics having high mechanical strength by the sintering via pressing of these powders.

ACKNOWLEDGMENT

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