

## CHARACTERISATION OF FINE ALUMINA POWDERS OF MAXIMUM POROSITY PREPARED BY EMULSION EVAPORATION

Y. SARIKAYA, T. ALEMDAROĞLU, M. ÖNAL

*Department of Chemistry, Faculty of Science, Ankara University, Ankara, TURKEY*

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### ABSTRACT

Water in oil emulsions were prepared by  $\text{Al}(\text{NO}_3)_3$  solutions having various concentrations between 0.25 – 2.00 M. The emulsion droplets were investigated by optical microscopy. Infinitely stable emulsions were evaporated by dropping them into hot mineral oil. The precipitated dark brown precursors were calcined at 1000°C and fine alumina powders were obtained. Adsorption and desorption of nitrogen on the powders was realized at 77K. The specific surface areas (A) and the specific micropore-mesopore volumes (V) were determined respectively from the data of adsorption and desorption. The variation of the A and V values as a function of the concentration of  $\text{Al}(\text{NO}_3)_3$  solutions was determined. The powder which had the maximum A and V values, was characterised by taking its photograph by an electron microscope and also by determining its particle size distribution and mesopore size distribution.

### KEYWORDS

Alumina Powder, Calcination, Emulsion, Particle Size Distribution, Pore Volume, Pore Size Distribution, Porosity, Surface Area.

## 1. INTRODUCTION

Conventional ceramics used in our daily lives are produced from natural industrial raw materials. The raw materials of high technology ceramic materials used in industry are specially prepared from chemicals of high purity<sup>1</sup>. The first and most important step in the production of such ceramics is the production of spherical and smallest possible fine ceramic powders<sup>2</sup> since, during the forming, the closest spherical packing can only be achieved with powders having such characteristics<sup>3</sup>. Powders of different shapes and sizes and agglomeration of particles affect the formation of the closest spherical packing in the opposite sense. As the closest spherical packing ratio during the forming increases, the density of the ceramic material obtained as a result of sintering, increases and approaches to its theoretical value<sup>4</sup>. The mechanical strengths of ceramic materials whose densities

are close to the theoretical value, attain their maximum values. This situation is particularly important in the case of structural ceramic materials.

In ceramic materials whose densities approach to their maximum values, the porosity approaches to minimum. In industry, besides ceramic materials which have minimum porosities, ceramic materials which have porosities of varying degrees are also used. Especially, ceramic materials which are prepared to serve as filters, catalyst beds, nuclear fuels are required to be porous. The pores which arise from the empty spaces in the ceramic materials have different shapes and sizes. The pores are assumed to be cylindrical and those having radii smaller than 1 nm are called micropores, those having radii between 1 –25 nm are called mesopores and those having radii greater than 25 nm are called macropores<sup>5</sup>. The porosities of the ceramic materials vary depending on the shapes, sizes and porosity of the fine powders as well as the parameters of shaping and sintering<sup>6</sup>. During the forming by pressing, the kind of pressing and the pressure of pressing change the porosity. On the other hand, the porous structure can be adjusted as required by varying the time and temperature of sintering. It was experimentally demonstrated that, the macropores between the particles were transformed into mesopores when the pressure of pressing was increased. The pressure of pressing did not affect the macropores which are inside the particles. It was also demonstrated that the mesopores which were between and inside the particles were transformed into micropores and the already existing micropores disappeared by increasing either the temperature or the time of sintering. The macropores inside the particles did not undergo much transformation during the sintering.

As is mentioned above, the porosities of ceramic materials depend considerably on the shapes, sizes and porosities of the fine ceramic powders used. The porosity of the fine powders varies depending on the chemical structure, crystal structure, preparation method and calcination temperature. Among the high technology ceramics, alumina is one of the most used ceramic material<sup>7,8</sup>. One of the methods used for the preparation of fine powders for the production of alumina is emulsion evaporation<sup>9</sup>. The aim of this study was to prepare and characterise fine alumina powders of maximum porosity by emulsion evaporation.

## 2. MATERIALS AND METHOD

White mineral oil (AMOCO, 21 USP), non ionic emulgator (ICI Americas, Arlachel 83) and analytically pure Al (NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (Merck) were used for the preparation of the emulsions.

0.25; 0.50; 1.00; 1.50; 1.75 and 2.00 M Al (NO<sub>3</sub>)<sub>3</sub> solutions were prepared. Infinitely stable, six different emulsions were prepared by mixing 65 % mineral oil, 30 % Al (NO<sub>3</sub>)<sub>3</sub> solution and 5 % Arlachel 83 (represented as volume %), according to the optimum conditions determined in our previous studies<sup>10,11</sup>. The prepared emulsions were investigated by optical microscopy. The emulsions were successively evaporated by dropping them into mineral oil at 240 °C. The dark

brown alumina precursors were separated by a centrifuge (Beckman TJ – 6) at a frequency of  $2500 \text{ min}^{-1}$ . In order to eliminate any mineral oil or Arlacel 83 left, the precursors were washed several times with toluene. The precursors were dried in an oven with fan, for 24 hours, and were stored in polyethylene bags.

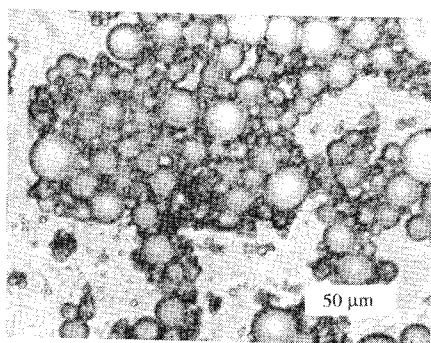
The precursors whose organic compounds were eliminated by combustion were calcined at  $1000 \text{ }^\circ\text{C}$  for 2 hours and fine alumina powders were obtained. The data of adsorption and desorption of nitrogen on the powders were determined at the temperature of liquid nitrogen. A volumetric adsorption instrument which was connected to high vacuum and fully constructed of pyrex glass was used in the experiments<sup>12</sup>. It was determined from the adsorption and desorption data that, the powder which was prepared by using  $1.00\text{M Al(NO}_3)_3$  solution was composed of particles of maximum porosity.

The particle size distribution of the powder which had maximum porosity was determined by a light scattering particle size analyzer (Leeds and Nothrup, Microtrac SPA). The shapes, sizes and porosities of these particles were investigated by a scanning electron microscope (JOEL JSM-U3).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterisation of the Emulsion

The fact that the emulsions were spoilt in water showed that the emulsion of the droplets was water in oil type. The photograph, taken by an optical microscope, of the droplets in the emulsion which was prepared by using a  $0.50 \text{ M Al(NO}_3)_3$  solution is given in Figure 1. It can be clearly observed from this photograph that the spherical droplets are of very different sizes. The hydrophilic groups and the hydrophobic groups of the Arlacel 83 emulgator attract, respectively, the water molecules and the mineral oil molecules and thus facilitate the formation of the spherical droplet.

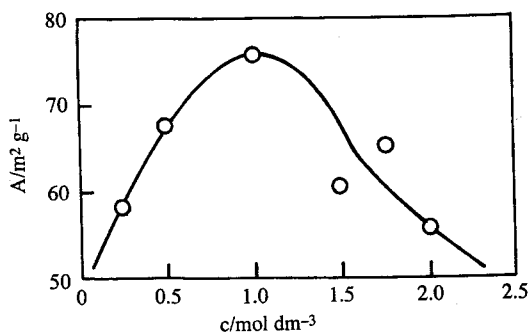


**Figure 1.** The emulsion droplets which were prepared by using  $0.50 \text{ M Al(NO}_3)_3$  solution, under the optimum conditions.

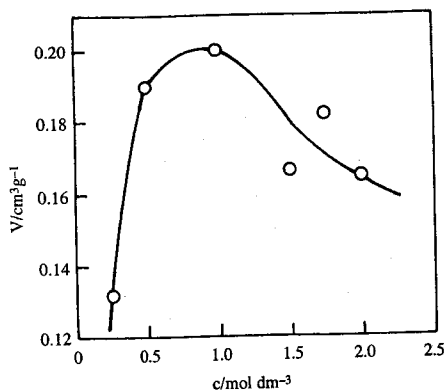
### 3.2. Porosity of the Powders

In our previous studies, it was determined that the precursor which formed during the emulsion evaporation contained diaspore ( $\beta$ -AlOOH) as raw alumina and the fine alumina powders were  $\alpha$ -Al<sub>2</sub>O<sub>3</sub><sup>13</sup>.

The specific surface areas (A) of the powders were determined according to the Brunauer-Emmett-Teller (BET) procedure, from the data of the adsorption of nitrogen at 77K<sup>14</sup>. The variation of A as a function of the concentration (c) of Al(NO<sub>3</sub>)<sub>3</sub> solution is given in Figure 2. The specific micropore-mesopore volumes (V) which were assumed to be equal to the adsorption capacity (i.e. the volume of liquid nitrogen) were determined from the data of desorption<sup>5</sup>. The variation of V as a function of c is given in Figure 3. From the graphs of A-c and V-c, it was observed that the A and V values, respectively reached a maximum at  $c = 1.00 \text{ mol dm}^{-3}$ . This situation showed that the most porous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> particles could be prepared by using 1.00 M Al(NO<sub>3</sub>)<sub>3</sub> solution.



**Figure 2.** The variation of the specific surface area of the fine alumina powders as a function of the molarity of Al(NO<sub>3</sub>)<sub>3</sub> solution.



**Figure 3.** The variation of the specific micropore-mesopore volume as a function of the molarity of Al(NO<sub>3</sub>)<sub>3</sub> solution.

The adsorption capacity at each relative equilibrium pressure was calculated as the volume of liquid nitrogen, from the data of desorption. These values were taken as the total specific volume of the micro and mesopores which were not yet empty at the given relative equilibrium pressure. On the other hand, among the mesopores which were assumed to be cylindrical and which were not yet empty at each relative equilibrium pressure, the radius ( $r$ ) of the largest one was calculated from the corrected Kelvin equation <sup>5</sup>. For the powder of maximum porosity, the mesopore size distribution curve  $(dV/dr) - r$ , which gives the radius derivative of the specific micropore-mesopore volume as a function of mesopore radii, is shown in Figure 4. From the maximum of this curve, the average mesopore size,  $\langle r \rangle$ , is determined as 1.8 nm.

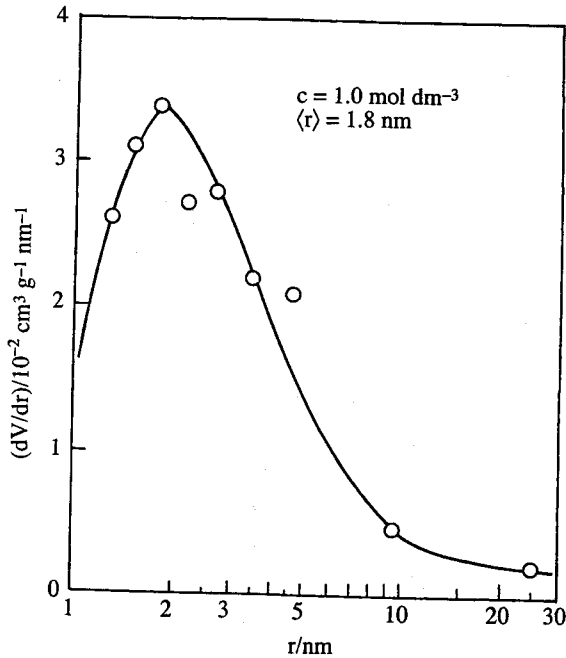
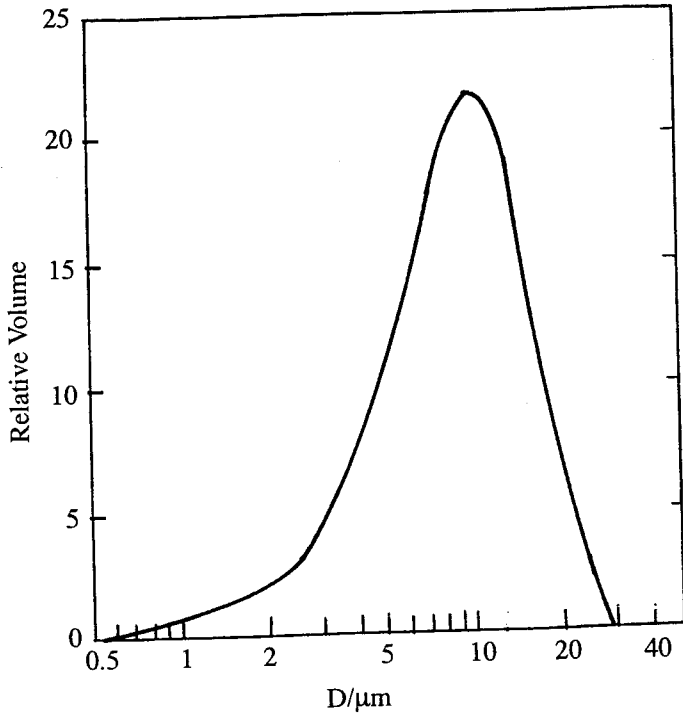


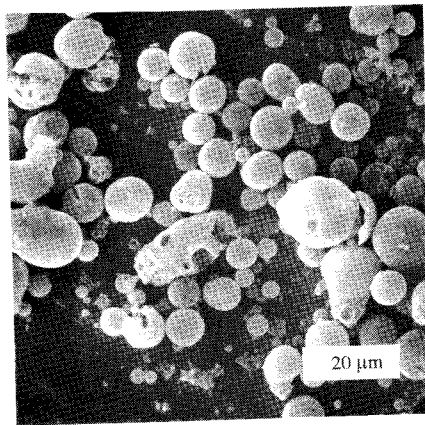
Figure 4. The mesopore size distribution curve of the alumina powder of maximum porosity.

### 3.3. The Sizes and Shapes of the Powders

The particle size distribution of the fine alumina powders of maximum porosity is given in Figure 5. It can be clearly observed from this figure that the particle size varies between 0.6 – 30  $\mu\text{m}$  and the average particle size is around 10  $\mu\text{m}$ .

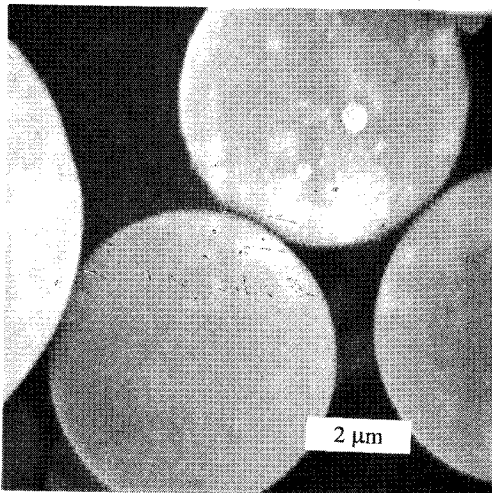


**Figure 5.** The particle size distribution curve of the alumina powder of maximum porosity.



**Figure 6.** The shapes, sizes and pore structures of the particles in the alumina powder of maximum porosity in the photograph taken by an electron microscope.

The photograph, taken by an electron microscope, of the fine alumina powders of maximum porosity is given in Figure 6. It is observed from this photograph that the particles were of very different sizes. It was observed that the average particle sizes determined from this figure and from Figure 5, respectively, were in good correlation. From figure 6, it was observed that some of the particles were in the form of regular spheres, some were in the form of burst spheres and some were in the form of agglomerated and burst spheres. Therefore it was understood from this figure that the fine alumina powders were porous. The pores seen in Figure 6 are macropores. The meso and micropores which are effective in adsorption are smaller and are not perceptible in a photograph of this magnification. Some of the regular spherical particles are shown in Figure 7. It was observed that, very small spherical particles were placed on the surfaces of big spherical particles.



**Figure 7.** The photograph, taken by an electron microscope, of the equally sized and completely spherical particles in the alumina powder of maximum porosity.

#### 4. CONCLUSION

It was understood that the fine  $\alpha\text{-Al}_2\text{O}_3$  particles were formed of unequally sized porous particles. It was observed that the particles were formed of shells in the forms of regular spheres, deformed spheres and agglomerated spheres. It was concluded that the fine  $\alpha\text{-Al}_2\text{O}_3$  particles could be used in the production of abrasives, adsorbents, filters and catalyst beds.

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