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Determination of the shape, size and porosity of fine α-Al_2O_3 powders prepared by emulsion evaporation

Yüksel Sarikaya*, Tülay Alemdaroğlu, Müşerref Önal

University of Ankara, Faculty of Science, Department of Chemistry, Tandodan, 06100 Ankara, Turkey

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Abstract

Stable water in oil emulsions were prepared from $Al(NO_3)_3$ solutions of different molarities. Dark brown precursors were obtained from these emulsions which were evaporated by adding them dropwise into hot mineral oil. The precursors containing diaspore as raw alumina were calcined at 1000 °C and fine α-Al_2O_3 powders were obtained. The photographs of the powders were taken by the use of an electron microscope and their particle size distributions were determined. The shapes and sizes of the powders were discussed. Their mesopore size distributions were obtained from the data of the desorption of nitrogen at 77 K. The relation between the obtained results and the concentrations of the $Al(NO_3)_3$ solutions were discussed. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The first and most important step in the production of high technology ceramics is the preparation of fine ceramic powders.[1,2] These powders have to be formed of small and equally sized spheres since this is the necessary condition for the closest spherical packing during the slip casting and forming by pressing.[3]

Ceramic materials whose densities are close to the theoretical value can be produced by sintering of the bodies which are formed by the closest spherical packing of nonporous spherical particles.[4] These kinds of ceramics which have high mechanical strength are mostly used in the production of machine parts.

On the other hand, ceramic materials which are used as filters, catalyst beds and nuclear fuels have to be porous. The densities of these kinds of materials are lower than the theoretical value. The porosity of these kinds of materials can be adjusted by changing the conditions of the production of fine powders, the pressure of pressing and the temperature of sintering. Inside the powder particles and between the powder particles, there are macropores whose widths are greater than 50 nm. There are also mesopores whose widths vary between 2 and 50 nm as well as micropores whose widths are smaller than 2 nm inside the powder particles. The macropores which exist between the particles can be decreased to a minimum or can be completely eliminated by increasing the pressure of pressing, whereas in the case of the mesopores and micropores which are inside the particles the same purpose can be realized by increasing the temperature of sintering.[5] The transmittance, catalytic, optical, thermal, mechanical, electrical and magnetic properties of ceramic materials depend extensively on their pore structures.

Alumina is the principle material among the ceramic materials that can be produced as both porous and nonporous.[6] One of the unconventional methods used in the production of fine alumina powders as well as other ceramic powders is the technique of emulsion evaporation.[7–10] The aim of this study was the determination of the shape, size and porosity of α-Al_2O_3 powders prepared by this technique.

2. Materials and method

White mineral oil (AMOCO, 21 USP), non ionic Arlacel 83 (ICI Americas) emulgator and analytically pure $Al(NO_3)_3.9H_2O$ (Merck) were used in the preparation of

* Corresponding author. Tel.: +90-312-212-67-20 ext. 1164; fax; +90-312-223-23-95.
E-mail address: sakaya@science.ankara.edu.tr (Y. Sarikaya).

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emulsions. $Al(NO_3)_3$ solutions of 0.25; 0.50; 1.00; 1.50; 1.75 and 2.00 M concentrations were prepared.

Stable emulsions were prepared under the optimum conditions determined in previous studies[11,12] by mixing 65% mineral oil, 30% $Al(NO_3)_3$ solution and 5% Arlacel 83 (all represented in% by volume). Water in oil emulsions were investigated by optical microscopy.

The emulsions which were obtained by using $Al(NO_3)_3$ solutions having the above given concentrations were successively evaporated by adding them dropwise into the mineral oil whose temperature was 240 °C. The dark brown precursors observed as a result of each evaporation were separated by a centrifuge (Beckman TJ-6) at a frequency of 2500 min^{-1}. The precursors were washed several times by toluene and were dried for 24 h in a furnace at 240 °C. The 6 precursors thus obtained were stored in polyethylene bottles.

In our previous studies it was determined that these precursors contained 70% organic matter and 30% diaspore (β-AlOOH).[13] Twenty gram specimens taken from each precursor were successively heated in a crucible until their color became white. During this period, it was observed that the organic matter evaporated at first then burned and was eliminated completely at 550 °C. The rest was calcined for 2 h at 1000 °C and thus, fine alumina powders were obtained.[14] In our previous study, it was determined by X-ray diffraction that these powders were α-Al_2O_3.[13]

The photograph of the prepared powders was taken by an electron microscope (Jeol, JSM U-3). The particle size distribution (PSD) of the same powders was determined by a light scattering particle size analyzer (Leeds and Northrup, Microtrac SPA).

The adsorption and desorption of nitrogen on the powders, at the temperature of liquid nitrogen, was performed by a volumetric adsorption instrument connected to high vacuum, constructed completely of Pyrex glass.[15]

3. Results and discussion

3.1. Characterisation of the emulsion

The magnified photograph of a stable emulsion droplet which was prepared under the optimum conditions by using a 0.25 M $Al(NO_3)_3$ solution is given in Fig. 1. The Arlacel 83 emulgator attracts the mineral oil by its hydrophobic groups and attracts the water by its hydrophyllic groups and facilitates the formation of the spherical droplet.

The emulsion is of water in oil type since it is not destroyed in oil but is destroyed in water. Therefore, there is an $Al(NO_3)_3$ solution in the inside, and mineral oil on the outside of the emulsion droplet. The diameter of the emulsion droplet seen in Fig. 1 was 13 μm. The investigated droplet is one of the biggest droplets in the emulsion. From many photographs, the average diameter of the droplets for the investigated emulsion was $d = 4.5$ μm.

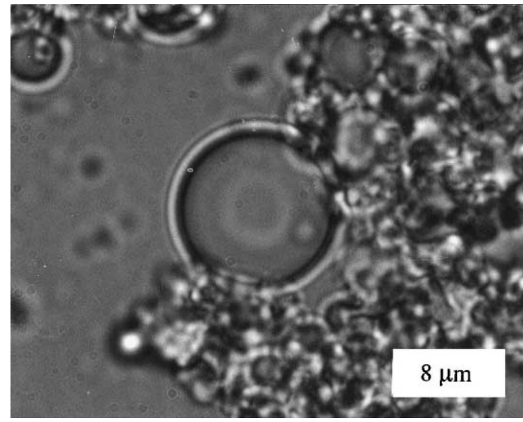

Fig. 1. A photograph, taken by an optical microscope, of the droplets in an emulsion which was prepared by using a 0.25 M Al $(NO_3)_3$ solution.

The photograph of a stable emulsion droplet which was prepared under the optimum conditions by using a 0.5 M $Al(NO_3)_3$ solution is given in Fig. 2. It can be clearly observed in this figure that droplets with a large range of diameters are formed. The average diameter of the droplets for the investigated emulsion was $d = 8.0$ μm.

In our previous study, it was determined that, as the concentration of the $Al(NO_3)_3$ solution increased, the average diameter of the droplets increased at first, then passed through a maximum and then decreased.[12]

3.2. Characterisation of the powders

The photograph of the α-Al_2O_3 powders which were obtained by the evaporation of the emulsion which was prepared by using a 0.25 M $Al(NO_3)_3$ solution is given in Fig. 3. It can be observed from this photograph that the

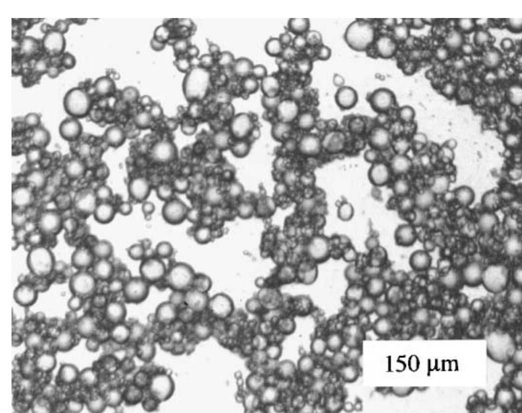

Fig. 2. A photograph, taken by an optical microscope, of the droplets in an emulsion which was prepared by using a 0.50 M Al $(NO_3)_3$ solution.

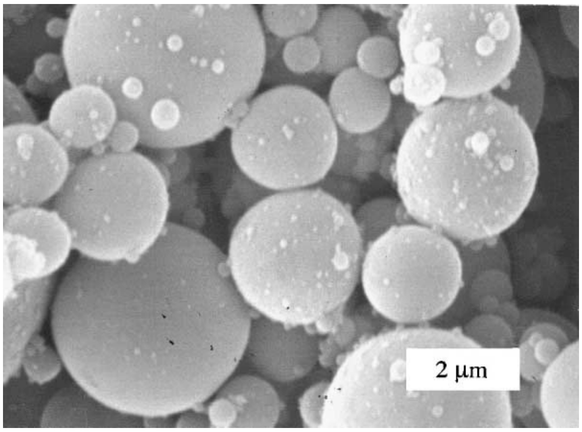

Fig. 3. A photograph, taken by an electron microscope, of α-Al_2O_3 powders which were prepared by the evaporation of an emulsion which was prepared by using a 0.25 M Al $(NO_3)_3$ solution.

α-Al_2O_3 powders are composed of spherical particles of varying sizes. Furthermore, agglomerated, broken and nonspherical particles are not observed. The average diameter (D) of these spheres which were formed during the evaporation of the emulsion whose average diameter was 4.5 μm, was calculated as 3.0 μm. In fact, the formation of a much smaller particle would be expected from the thermal decomposition of a small amount of $Al(NO_3)_3$ in an emulsion droplet whose diameter is 4.5 μm. The small difference between the diameter of the droplet and the diameter of the particle can be explained either by the occurrence of high porosity inside the particles or by the occurrence of particles in the form of hollow spherical shells.

The photograph of the α-Al_2O_3 powders which were obtained by the evaporation of the emulsion which was prepared by using a 0.50 M $Al(NO_3)_3$ solution is given in Fig. 4. In this photograph it is observed that some of the α-Al_2O_3 particles which are not of equal size and form, have burst. It can be clearly observed that the particle which has burst is a hollow spherical shell. It is also observed that particularly big particles are non spherical. The average diameter of these particles which were formed from emulsion droplets whose average diameters were 8.0 μm, is calculated from the photographs to be 5.5 μm.

The photograph of a broken up particle among the α-Al_2O_3 powders which were obtained by the evaporation of the emulsion which was prepared by using a 0.50 M $Al(NO_3)_3$ solution is given in Fig. 5. It is observed that the shell of the particle is very porous and the middle of the particle is empty, such that a smaller particle had entered into this empty space. The average diameter of these particles which were formed from emulsion droplets whose average diameters were 8.0 μm, is calculated from the photographs to be 8.0 μm. As was mentioned above, it was concluded that the equality of the average diameters of the emulsion droplets and of the particles was due to the presence of spherical shells of high porosity inside the particles.

It was determined that the average particle diameter reached a maximum when the concentration of the $Al(NO_3)_3$ solution was 1.50 M and then decreased at higher concentrations.[12]

The particle size distribution (PSD) curves of the α-Al_2O_3 powders which were prepared by using 0.25, 0.50 and 1.50 M $Al(NO_3)_3$ solutions are given in Fig. 6. It is observed that the particles get bigger as the concentration of the $Al(NO_3)_3$ solution increases. If the concentration increases further than 1.5 M (not given in Fig. 6) the particle size distribution shifts towards the left, i.e. the particles get smaller again.[12] The values corresponding to the maxima of the PSD curves are taken as the average particle diameter. The average particle sizes of the 0.25, 0.50 and 1.50 M solutions are

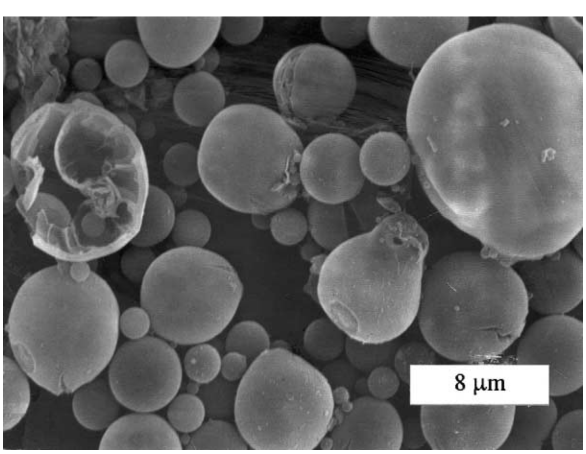

Fig. 4. A photograph, taken by an electron microscope, of α-Al_2O_3 powders which were prepared by the evaporation of an emulsion which was prepared by using a 0.50 M Al $(NO_3)_3$ solution.

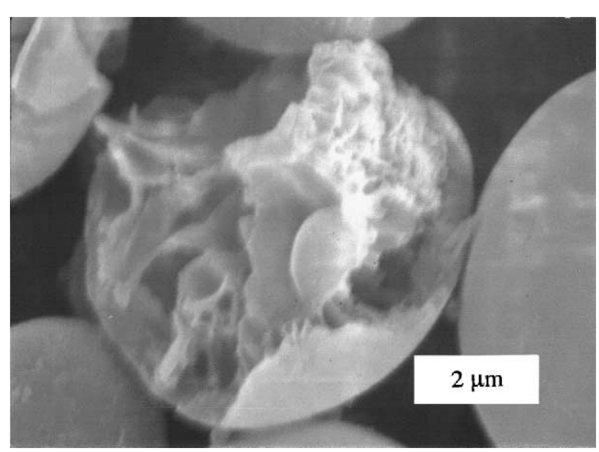

Fig. 5. A photograph, taken by an electron microscope, of a broken up α-Al_2O_3 particle which was obtained by the evaporation of an emulsion which was prepared by using a 0.50 M Al $(NO_3)_3$ solution.

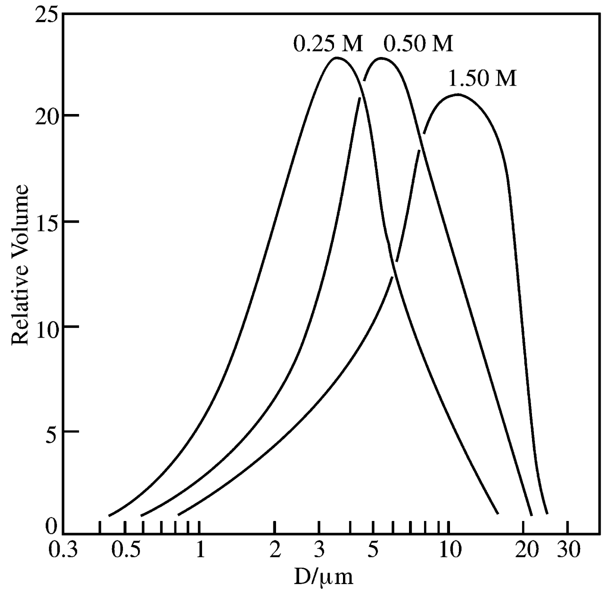

Fig. 6. The particle size distribution curves of α-Al_2O_3 powders which were obtained by the evaporation of the emulsions which were prepared by using Al $(NO_3)_3$ solutions of three different concentrations.

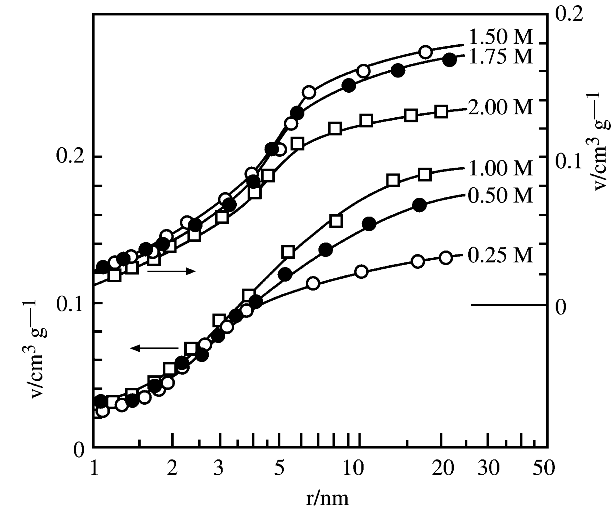

Fig. 7. The mesopore size distribution curves of α-Al_2O_3 powders which were obtained by the evaporation of the emulsions which were prepared by using Al $(NO_3)_3$ solutions of six different concentrations.

determined respectively as 3, 5 and 10 μm. It can be stated that there is a good correlation between these values and the values determined previously from the photographs.

3.3. Porosity

Although only the macropores but not the mesopores and micropores can be observed clearly in the photographs of the given magnification taken by electron microscopy, the micropore and mesopore surfaces are very active whereas macropore surfaces are nonactive. Besides, the adsorption capacity of the macropores is negligible when compared to that of the mesopores and micropores. Therefore, only the meso and microporosity of the α-Al_2O_3 powders will be examined here by the help of the pore size distribution curves.

The *v–r* mesopore size distribution curves which are plotted by the help of the corrected Kelvin equation [16] by using the data of desorption of nitrogen at 77 K are given in Fig. 7. Here, *r* represents the radii of the pores which are assumed to be cylindrical and *v* represents the specific micropore–mesopore volumes which is taken to be equal to the volume of liquid nitrogen that is left in one gram of powder during the desorption.[17,18]

It can be clearly observed from Fig. 7 that the specific volume of the micropores whose radii approach to 1 nm, are the same and equal to approximately 0.02 $cm^3\ g^{-1}$ for all of the powders. It is also observed from Fig. 7 that, similar to the specific volume of the micropores, the specific volume of the mesopores whose radii are smaller than 4 nm does not vary considerably depending on the concentrations of the $Al(NO_3)_3$ solutions. The specific volume of the mesopores whose radii vary between 4 and 25 nm increases at first as the concentration of the $Al(NO_3)_3$ solution increases and decreases after reaching a maximum at 1.0 M, corresponding to a value of 0.20 $cm^3\ g^{-1}$. According to this determination, α-Al_2O_3 of highest porosity can be obtained by the evaporation of the emulsion which is prepared by 1.0 M $Al(NO_3)_3$ solution.

4. Conclusion

It was understood that α-Al_2O_3 powders in the form of spheres of high mesoporosity or in the form of hollow spherical shells, could be prepared by the technique of emulsion evaporation. It was observed that the mesoporosity of those powders was low and their microporosity was at a negligible level. It was determined that, in addition to the sizes of particles and emulsion droplets the mesoporosity as well showed variations with concentration in such a way that each gave rise to a maximum. It was understood that, as the concentration of the solution increased, the particles lost their spherical forms and were broken into pieces more easily. It was concluded that the quality of the α-Al_2O_3 powders obtained by the emulsion evaporation technique was suitable for their use as abrasives, filters, column support materials and catalyst beds.

Acknowledgements

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