Turk J Chem
25 (2001) , 283 – 291.
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Determination of Some of the Physicochemical Properties of Fine Alumina Powders Prepared by Emulsion Evaporation

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Received 13.06.2000

In order to prepare fine alumina powders, an emulsion was prepared under optimum conditions. The emulsion was examined by optical microscopy and the prepared fine alumina powders were characterised by electron microscopy. The particles were formed of porous spheres and their sizes were between 1 and 10 μm. The powder samples were sintered by varying the temperature between 700 and 1600°C. The adsorption and desorption of nitrogen on these samples were investigated. By using the adsorption data, the specific surface areas were calculated according to different procedures and the correlation between them was discussed. The specific micropore and mesopore volumes were calculated from the desorption data. Some kinetic and thermodynamic estimations about the intra-particle sintering were made according to the variation of the specific micropore-mesopore volumes as a function of the sintering temperature.

Key Words: Alumina powder, calcination, pore volume, sintering, surface area, thermal analysis.

Introduction

The first and most important step in the production of high technology ceramics is the preparation of fine ceramic powders from pure chemical reagents[1,2]. The calcined powder particles are expected to be in closely packed structures and it is necessary that they are spherical, equally sized, as small as possible and inagglomerated during the shaping process[3–5].

The empty spaces in calcined powder particles and in sintered materials are called *pores.* The pores are generally assumed to be cylindrical. A pore whose radius (r) is smaller than 1 nm is called a *micropore*, one whose radius is between 1 nm and 25 nm is called a *mesopore* and one whose radius is bigger than 25nm is called a *macropore* [6,7]. The density and the mechanical, permeability, thermal, magnetic, electrical, optical and catalytical characteristics of ceramics vary considerably as a function of their pore structures.

One of the unconventional methods for the preparation of fine ceramic powders is the *emulsion evaporation technique* [8–11]. The conditions for the preparation of aqueous solution in oil type emulsions by Al^{3+} solutions were determined in our previous studies[12]. The effects of the solution/oil ratio and evaporation temperature on the adsorption characteristics of fine alumina powders were investigated and the optimum conditions for the evaporation process were determined [13]. The thermal decomposition kinetics of the precursor, which was obtained by emulsion evaporation, was discussed and it was determined that the raw alumina which was formed in the precursor was diaspore (β-AlOOH) and it was transformed into α-Al_2O_3 at temperatures above 550^{o}C [14]. The inter-particle and intra-particle sintering was not investigated in our previous studies. It was thought that it would be possible to derive some information about the intra-particle sintering by determining the adsorption characteristics. Therefore, the aim of this study was to determine some of the physicochemical properties such as the particle size, particle size distribution, adsorption characteristics, sintering kinetics and the sintering thermodynamics of the fine alumina powders obtained by the sintering of the precursor at various temperatures between 700 and 1600°C.

Materials and Methods

Analytically pure $Al(NO_3)_3.9H_2O$ (Merck) was used to prepare 2M $Al(NO_3)_3$ stock solution. According to the optimum conditions previously determined, an infinitely stable emulsion of the type aqueous solution in oil was prepared by mixing 65% by volume mineral oil (AMOCO,21 USP), 30% by volume 2M $Al(NO_3)_3$ solution and 5% by volume Arlacel 83 (ICI Americas) emulsifier [12,13]. The prepared emulsion was investigated by optical microscopy. At the end of evaporation, a dark brown precursor was formed in hot oil . It was separated by centrifugation for 30 min at a rate of 2500 min^{-1} in a Beckmann TJ-6 Instrument. The precursor was washed several times with toluene and was dried at 240°C for 24 hours. It was then stored in a plastic bottle.

The photographs of the fine alumina powders calcined at 1000°C, in air, for 2 hours, were 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 analyser (Leeds and Northrup, Microtrac SPA).

The data of the adsorption and desorption of nitrogen, at liquid nitrogen temperature, on the powders which were obtained by heating the alumina precursor for 2 hours at temperatures between 700 and 1600°C were determined. A volumetric adsorption instrument fully constructed of Pyrex which was attached to a high vacuum system, was used in the experiments[15].

Results and Discussion

Characterisation of Powders

The photograph of the emulsion droplets which were prepared under optimum conditions is given in Figure 1. It can be clearly observed that, although the emulsion droplets are spherical, they are not of equal size. The white mineral oil membrane around the droplets and the 2M $Al(NO_3)_3$ solution inside the droplets are kept together by the hydrophobic and hydrophilic groups of the Arlacel 83 emulsifier. The precursor was obtained by the evaporation of the above emulsion and the fine alumina powders were produced by the calcination of the precursor, for 2 hours at 1000°C. The photograph of the fine alumina powders is given in Figure 2. It was determined that very small diaspore (β -AlOOH) particles were formed from the solution which was inside the droplets, which broke into pieces as soon as they fell into the hot mineral oil. The shapes and sizes of the α -Al_2O_3 powders, which were produced by the calcination of the precursor, can be seen in Figure 2. It is understood that unequally sized fine alumina powders were formed as a result of the decomposition by evaporation of the emulsion droplets which were also unequally sized. It is also observed that non-spherical, larger particles were formed by the interfusion of some particles with each other, and some of the particles were destroyed. The destruction of a particle can be clearly observed from the photograph seen in Figure 3.

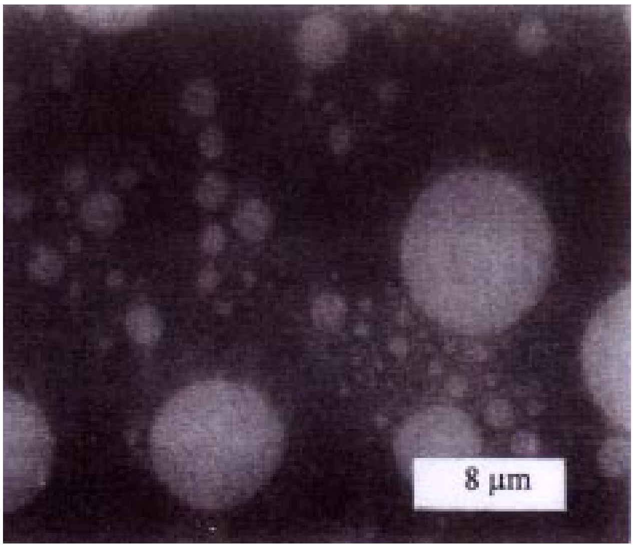

Figure 1. The photograph, taken by an optical microscope, of a water in oil emulsion prepared by 2M $Al(NO_3)_3$ solution under optimum conditions.

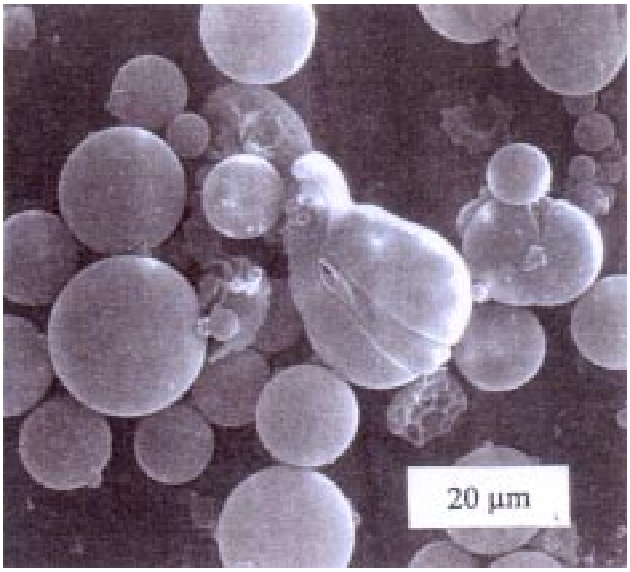

Figure 2. The photograph, taken by a scanning electron microscope, of the fine powders which were obtained by the calcination of the alumina precursor for 2 hours at 1000°C.

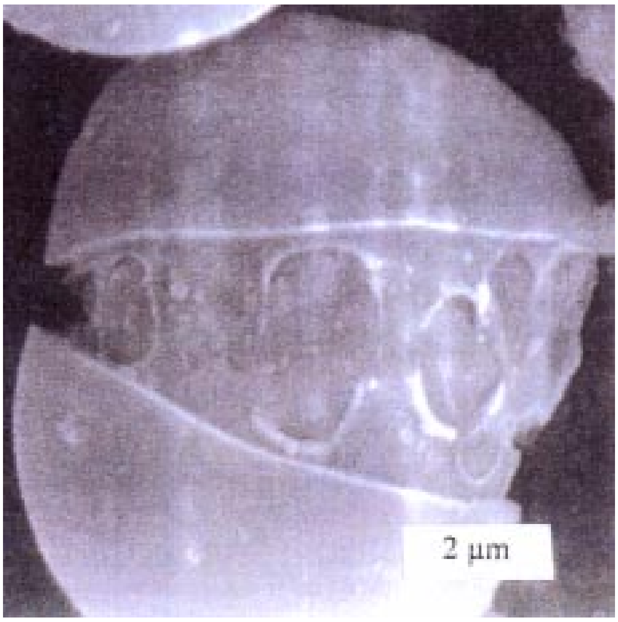

Figure 3. The photograph, taken by a scanning electron microscope, of an alumina particle which is being broken.

The PSD curve, which shows the variation of the relative volume of the calcined particles as a function of the particle size, is given in Figure 4. It can be observed from this curve that the average particle size was 7.5 μm. The distribution of the particle sizes in a large interval between 0.3 and 20 μm was related to the fact that the particles were unequally sized and to the occurrence of the interfusion and destruction of particles during the emulsion evaporation.

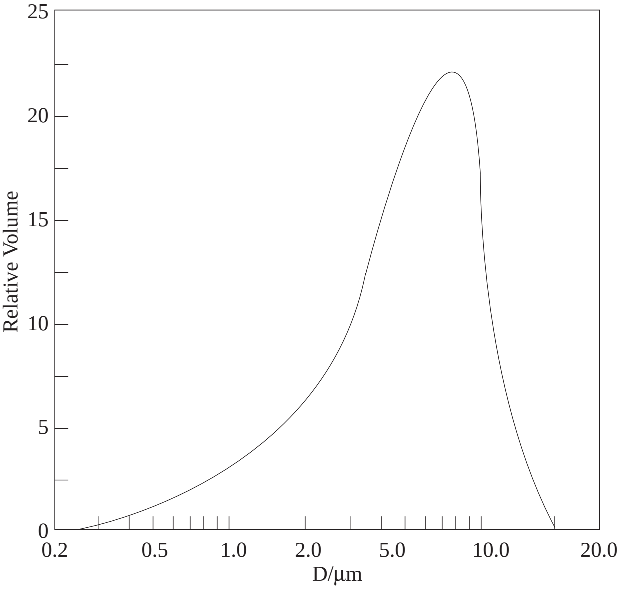

Figure 4. The particle size distribution of the fine powders which were obtained by the sintering of the alumina precursor for 2 hours at 1000°C.

Evaluation of the Nitrogen Adsorption and Desorption Data

The adsorption isotherms of the fine alumina powders, which were heated for 2 hours at different temperatures, are given in Figure 5. The p/p^0 is defined as the relative equilibrium pressure, where p is the equilibrium pressure of the adsorption and p^0 is the vapor pressure of liquid nitrogen, in the experimental environment. The adsorption capacity (v^g/cm^3g^{-1}) is taken as the normalized ideal gas volume at 273K and 1 atm of the nitrogen adsorbed on 1g of the alumina powders. The adsorption isotherms given in Figure 5 show the variation of the adsorption capacity as a function of the relative equilibrium pressure. It can be clearly observed from the adsorption isotherms that the adsorption capacity, which reached its maximum at the calcination temperature of 800°C, decreased rapidly at higher temperatures.

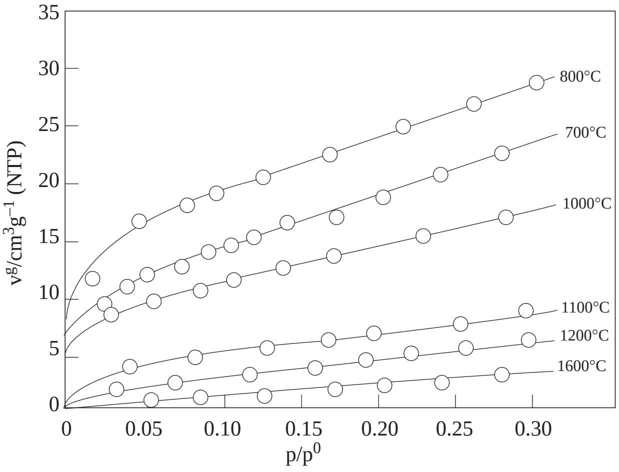

Figure 5. The isotherms, at the liquid nitrogen temperature, of the adsorption of nitrogen on the fine alumina powders which were heated at various temperatures for 2 hours.

The necessary capacity for the monomolecular coating of the micro and mesopore walls in one gram of the adsorptive substance is called a monolayer capacity (v_m^g/cm^3g^{-1}).

The monolayer capacity can be determined by one of the Langmuir (L), Brunauer-Emmett-Teller (BET) and Polonyi-Dubinin-Radusckevich-Kaganer (PDRK) methods and the specific surface area can be calculated according to the following equation[6]:

$$A/m^2g^{-1} = 4.35(v_m^g/cm^3g^{-1}) \tag{1}$$

The correlation between the surface areas calculated according to the L and PDRK methods[16], and the surface areas calculated according to the BET method, which is accepted as the standard method, is given in Figure 6. The good correlation between the specific surface areas determined respectively according to the L and PDRK methods which are valid for monomolecular adsorption, and the BET values, show that the adsorption of the fine alumina powders, which are calcined at various temperatures in the relative pressure interval $0 < p/p^0 < 0.30$, is monomolecular.

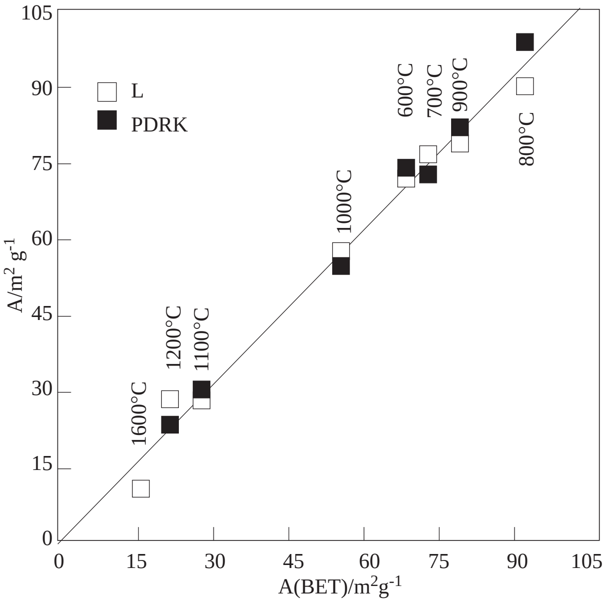

Figure 6. The correlation between the specific surface areas calculated according to different procedures, by using the data of the adsorption of nitrogen at liquid nitrogen temperature and the correlation between those and the values calculated according to the standard BET procedure.

The adsorption capacity (v^l_{mm}/cm^3g^{-1}), which is determined from the desorption data as the volume of liquid nitrogen at any relative equilibrium pressure, is taken to be equal to the specific volume of all of the micro and mesopores which are full at that relative equilibrium pressure. On the other hand, the radius (r) of the largest mesopore,which is full at any relative equilibrium pressure, and which is assumed to be cylindrical, can be calculated from the corrected Kelvin equation[6]. The v^l_{mm}-r graph, which gives the variation of the specific micropore-mesopore volume as a function of the pore radius is given in Figure 7a. The dv^l_{mm}/dr –r graph, drawn by taking the derivative of the previous graph which represents the pore size distribution curves of the fine alumina powders sintered at 700°C, is given in Figure 7b. By the extrapolation of the v^l_{mm}-r curve in Figure 7a to respectively r = 1nm and r = 25nm, the total specific micropore volume (v^l_{mi}) and the total specific micropore-mesopore volume (v^l_{mm}) of the fine alumina powder which was obtained at 700^{o}C, were respectively found to be equal to 0.015 cm^3g^{-1} and 0.132 cm^3g^{-1}. The average pore radius $< r >$, which corresponds to the maximum of the dv^l_{mm}/dr-r curve given in Figure 7b, was determined to be 2 nm. The v^l_{mm} values for the other samples were determined similarly, to be used in the kinetic and thermodynamic evaluations.

Kinetic and Thermodynamic Evaluations

Pellets were obtained by pressing the fine alumina powders under high pressure. During the heating of these pellets above 1000°C, intra-particle sintering and intra-particle sintering occur at the same time, whereas during the heating of the fine ceramic powders at the same temperatures, only intra-particle sintering occurs. The relative shrinking percentage, which can be easily determined during the sintering of pellets, cannot be determined during the direct sintering of powders. Most researchers make kinetic investigations assuming that there is a parallel variation between the temperature and the increases in the relative shrinkage, relative density and the rate constant$^{17-20}$. It is clear that the increases in the relative shrinkage and relative density can not be easily determined through direct heating of the powders. Therefore, in this study, it was thought that a kinetic investigation could be realized by assuming that there is a parallel variation between the relative decrease in the specific micropore-mesopore volume, which is an easily measurable quantity, and the sintering rate constant.

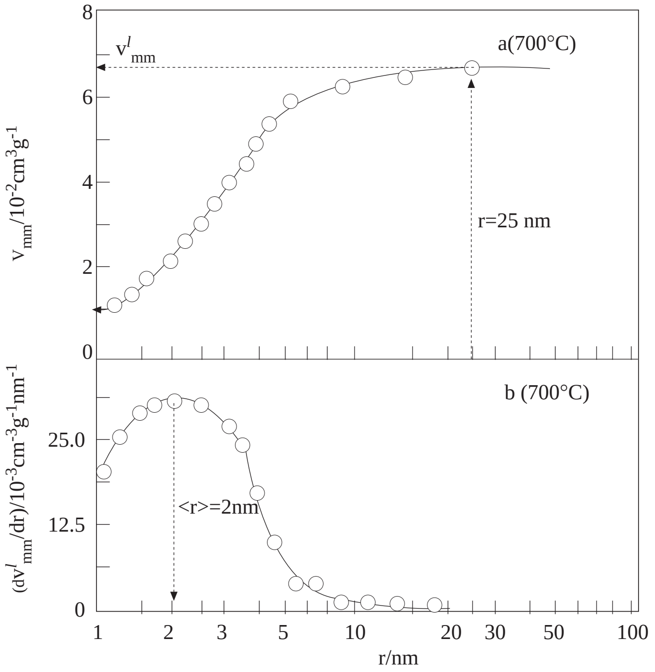

Figure 7. a) v^l_{mm}-r and b) dv^l_{mm}/dr-r pore size distribution curves which were determined from the desorption data.

The specific micropore–mesopore volume is believed to be proportional to the sintering rate constant. The relative decreasing percentages in the specific micropore-mesopore volume were calculated from the following relation:

$$k = 100[v^l_{mm}(1100) - v^l_{mm}]/v^l_{mm}(1100) = 100\Delta v^l_{mm}/v^l_{mm}(1100) \tag{2}$$

where the v^l_{mm} values of the powders which were heated at higher temperatures, and $v^l_{mm}(1100)$ value of the sample which was heated to 1100°C were used. When the logarithm of the k values were plotted as a function of the inverse of the absolute temperature, the straight line seen in Figure 8 was obtained. It was assumed that this line obeyed the following Arrhenius equation:

$$\ln k = -E/RT + c \tag{3}$$

The activation energy of sintering (E) was calculated as 28 kJmol^{-1} from the slope of this straight line. The fairly low activation energy indicates that the sintering inside the particles is a physical event.

In this study, the following quantity, which was thought to be proportional to the sintering equilibrium constant, was defined as the ratio of the relative decreasing percentage of the pore volume to the specific pore volume percentage left behind:

$$K = k/(100 - k) \tag{4}$$

The K constants at heating temperatures were calculated from this equation. The plot of lnK as a function of the inverse of the absolute temperature is given in Figure 9. The fact that this graph is a straight line shows that, similarly to the thermodynamic constant of sintering, the above defined K quantity, obeys the following van't Hoff equation:

$$\ln K = -\Delta H/RT + C \tag{5}$$

Here, ΔH is the enthalpy of sintering and C is a constant. The enthalpy of sintering was calculated to be 10 kJmol^{-1} from the slope of the straight line given in Figure 9. The fact that this value is rather low shows that the sintering progresses through physical events.

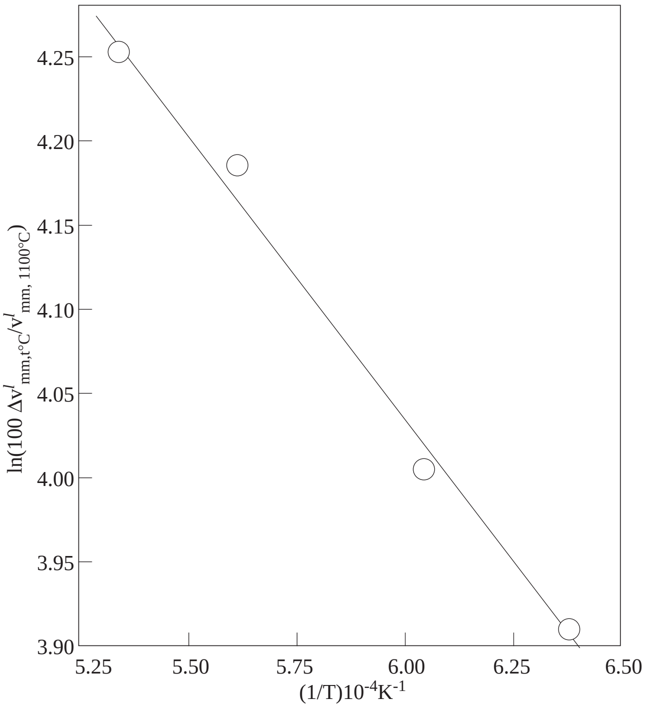

Figure 8. The Arrhenius straight line which shows the variation of a quantity, which is proportional with the sintering rate constant, as a function of the inverse of the absolute temperature.

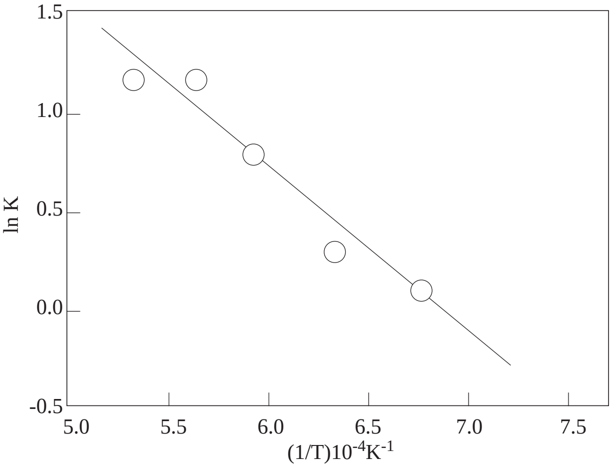

Figure 9. The van't Hoff straight line which shows the variation of a quantity which is proportional with the sintering equilibrium constant, as a function of the inverse of the absolute temperature.

Conclusion

It was observed that although the produced powders contained spherical or almost spherical particles, the particles were not equally sized. It was concluded that the fine alumina powders of considerably high porosity were suitable for use as catalyst beds.

It was observed that, for the powders produced in this manner, there was a good correlation between the specific surface areas determined according to the L, BET and PDRK methods. It was shown that it was possible to calculate the activation energy of sintering and the enthalpy variation through the relative decreasing percentage of the pore volume. It is believed that similar calculations can be performed by using the relative decreasing percentages of the surface area and the heat of adsorption.

Acknowledgement

The authors thank the Ankara University Research Fund who funded this work by the project No: 90 05 04 06.

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