

The Effect of Preparation Procedure for Precursor on the Morphology, Surface Area and Porosity of Alumina Powders

KEZBAN ADA

Department of Chemistry, Faculty of Arts and Sciences
Kirikkale University, Kirikkale, Turkey
E-mail: kezbanada@mynet.com

In order to investigate the effect of preparation procedure for precursors on some physico-chemical properties of powders, three alumina precursors were prepared by different ways. The first precursor (P1) was precipitated by adding ammonia to the boiling aluminium sulphate solution buffered by $\text{NH}_3/\text{NH}_4\text{Cl}$ (pH = 9.25). The second precursor (P2) was precipitated by the reaction between aluminium sulphate and excess urea in boiling aqueous solution (pH = 3.42). The third precursor (P3) was precipitated by the similar reaction in boiling aqueous solution buffered by $\text{C}_2\text{H}_4(\text{COOH})_2/\text{C}_2\text{H}_4(\text{COONH}_4)_2$ (pH = 4.16). Three different alumina powders (P1, P2 and P3) were obtained by the calcination of the precursors at 1000 °C for 2 h. The powders were examined by scanning electron microscopy and nitrogen adsorption-desorption techniques. The BET specific surface areas (A) and specific micro-mesopore volumes (V) for the powders (P1, P2 and P3) were obtained as 116 m² g⁻¹ and 0.34 cm³ g⁻¹, 66 m² g⁻¹ and 0.15 cm³ g⁻¹ and 148 m² g⁻¹ and 0.59 cm³ g⁻¹, respectively. The surface areas of the powders determined by other methods, are compared with the BET values.

Key Words: Alumina, Morphology, Pore volume, Precursor, Surface area.

INTRODUCTION

In the production of high technology ceramics, the first and the most important step is the preparation of same sized, same shaped and especially unagglomerated small spherical particles^{1,2}. Since, only the powders which have these properties can assure closest spherical packing during the shaping process. In this respect, many procedures have been developed³. Some of these non-conventional methods may be given as hydrothermal synthesis⁴, microwave synthesis⁵, emulsion evaporation⁶⁻⁹ and chemical precipitation from a solution¹⁰. In these methods, the required characteristics have been obtained by controlling the crystal type, crystal size, particle shape, particle size distribution, agglomeration degree, surface area and porosity¹¹⁻¹⁸.

Alumina powders have been extensively used in the production of ceramics, abrasives, medications, membranes, chromatographic column support materials, adsorbents and catalysts^{19,20}. Commercial alumina powders produced by the conventional Bayer technique did not possess the required characteristics for most of the high technology applications. Therefore, similar to the cases of other powders, many methods have been developed to prepare alumina powders²¹⁻²⁶. Besides density; mechanical permeability, thermal, electrical, optical and catalytical properties of ceramics depend considerably on their surface area and porosity. The porosity of ceramics varies depending on the type of pressing, pressing pressure, sintering temperature, sintering period and initial porosity of fine ceramic powders^{8,11,27}. The heating applied to precursor in order to eliminate the volatile is called calcination and the process in which firing is applied to the bonds of particles to change into a shaped specimen is called sintering^{8,11}.

The empty spaces in a solid whose widths are smaller than 2 nm, between 2 and 50 nm and greater than 50 nm are called micropores, mesopores and macropores, respectively^{28,29}. The radii of pores assumed cylindrical can be taken the half of widths. The contribution of macropore to the surface area may be negligible compared to the contribution of micro- and mesopores¹¹. The surface area and porosity may also be related to crystal type and morphology of alumina powders. The aim of this study was the determination of the differences for morphology, surface area and porosity of alumina powders depending on the preparation procedure of their precursors.

EXPERIMENTAL

Analytically pure aluminium sulphate, urea, ammonium chloride, succinic acid, nitric acid, (65 mass % and 1.40 g mL⁻¹) and ammonia, (35 mass % and 0.91 g mL⁻¹) were supplied by Merck Chemical Company. An aqueous stock solution of 0.4 M Al₂(SO₄)₃·18H₂O was prepared by adding of a small amount of nitric acid.

Preparation of precursors: A solution of 0.08 M Al³⁺, 200 mL prepared from the stock solution was buffered by NH₃/NH₄Cl in resulting pH of *ca.* 9.25. The first precursor (P1), Al(OH)₃, precipitated by the adding of an ammonia solution drop by drop on this boiling solution for 2 h.

A solution of 0.10 M Al³⁺, 800 mL was prepared from the stock solution. An excess amount of urea was added to establish the molarity ratio of [urea]/[Al³⁺] = 5.4. The pH value of the solution necessary for the precipitation of second precursor (P2), Al(OH)₃, is adjusted to 3.42 by adding an ammonia solution drop by drop^{25,26}. The P2 precipitated by boiling of this solution for 2 h.

A solution of 0.006 M Al³⁺, 800 mL was prepared from the stock solution and added an excess amount urea as above. This solution was buffered by

$C_2H_4(COOH)_2/C_2H_4(COONH_4)_2$ in resulting pH of *ca.* 4.16. The third precursor (P3), $Al(OH)_3$, was precipitated by boiling the solution for 2 h.

The precursors were filtered and washed with distilled water until free from Cl^- , NO_3^- and SO_4^{2-} ions. Three different alumina powders, labeled also as P1, P2 and P3, were obtained by calcination of the precursors at 1000 °C for 2 h.

The powders were investigated by using a Jeol-JSM U-3 Scanning Electron Microscope. The adsorption and desorption of nitrogen on the powders were realized at the liquid nitrogen temperature (*ca.* 77 K). A volumetric adsorption instrument constructed of Pyrex glass and connected to high vacuum was used by the experiments³⁰. Before the adsorption experiment, each powder was out gassed under vacuum at 150 °C for 4 h.

RESULTS AND DISCUSSION

The SEM photographs of the powders are given in Fig. 1. It can be clearly seen from SEM views that the shape and size of the particles in the powders depend on the preparation procedure of the precursors. The voids seen in SEM views are macropores. Meso- and micropores can not be seen in these SEM views. They are located almost in the particles.

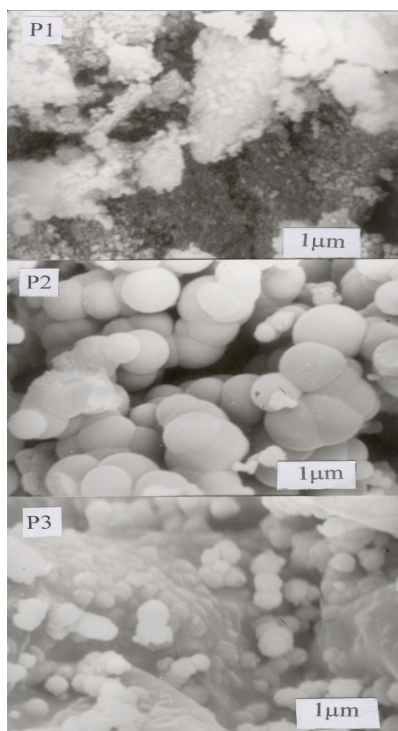


Fig. 1. Scanning electron microscope photographs of the alumina powders

The particles in the P1 powder are shapeless and their sizes are very different. The P2 powder contains agglomerates in different sizes which are formed from the spherical primary particles having a diameter of *ca.* 1.0 μm . There are spherical particles having diameter of 0.5 μm and agglomerates are formed from them in P3 powder.

Adsorption and desorption isotherms: The adsorption and desorption isotherms of nitrogen on the powders are given in Fig. 2. Here, p is the equilibrium pressure of the adsorption or desorption, p° is the saturated vapour pressure of liquid nitrogen, $p/p^\circ = x$ is the relative equilibrium pressure and $n/\text{mol g}^{-1}$ is the adsorption capacity defined as the amount of nitrogen adsorbed per 1 g of powder. The isotherms show that the adsorptions are multimolecular and the adsorption capacity depends on the preparation procedure of their precursors. The hysteresis loops between the adsorption and desorption isotherms are generally associated with capillary condensation and capillary evaporation. The capillary condensation begins in the smallest pore, whereas the capillary evaporation begins in the largest pore causes hysteresis.

Specific surface area: There are many methods for determining the specific surface area of powders and other porous materials by using nitrogen adsorption data. In this study, Brunauer-Emmett-Teller (BET), Lippens-de Boer (LB) and Harkins-Jura (HJ) methods were used. They are explained extensively in many books^{28,31,32}.

BET method: The BET equation derived for multimolecular adsorption is conveniently expressed in the linear form³³:

$$x/[n(1-x)] = 1/n_m c + [(c-1)/n_m c]x \quad (1)$$

where, $n_m/\text{mol g}^{-1}$ is the monomolecular adsorption capacity and c is a constant. BET plots of the powders drawn over the approximate range $0.05 < x < 0.35$ are given in Fig. 3. The n_m values of the powders were calculated by the solving two simultaneous equations obtained from slopes and intercepts of the BET straight lines. The specific surface areas ($\text{A}/\text{m}^2 \text{g}^{-1}$) are obtained by the application of the simple relation³²:

$$A = n_m L \sigma \quad (2)$$

where $L = 6.02 \times 10^{23} \text{ mol}^{-1}$ is Avogadro constant and $\sigma = 16.2 \times 10^{-20} \text{ m}^2$ is the average area occupied by each nitrogen molecule in the completed monolayer. The BET specific surface areas are given in Table-1.

Lippens-de Boer method: The standard multilayer thickness (t) of a close-packed nitrogen multilayer adsorbed on a non-porous reference material was calculated by the simple relation³⁴:

$$t/nm = (0.354/nm)n/n_m \quad (3)$$

where 0.354 nm is the thickness of a monolayer in the multilayer. The experimental nitrogen adsorption isotherm at 77 K on the reference material was transformed into a t -curve by plotting standard multilayer thickness (t)

TABLE-1
SPECIFIC SURFACE AREAS OBTAINED DIFFERENT PROCEDURE
AND SPECIFIC MICRO-MESOPORE VOLUMES OF THE
ALUMINA POWDERS

Sample	A_{BET} ($m^2 g^{-1}$)	A_{LB} ($m^2 g^{-1}$)	A_{HI} ($m^2 g^{-1}$)	V ($cm^3 g^{-1}$)
P1	115.6	116.1	113.7	0.34
P2	66.4	67.3	65.2	0.15
P3	148.4	150.8	143.8	0.59

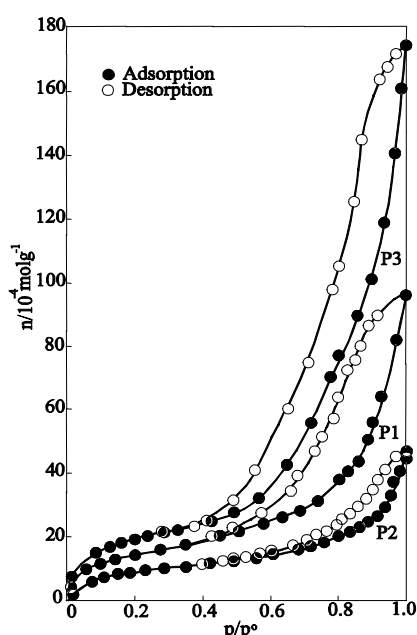


Fig. 2. Adsorption and desorption isotherms of nitrogen on the alumina powders

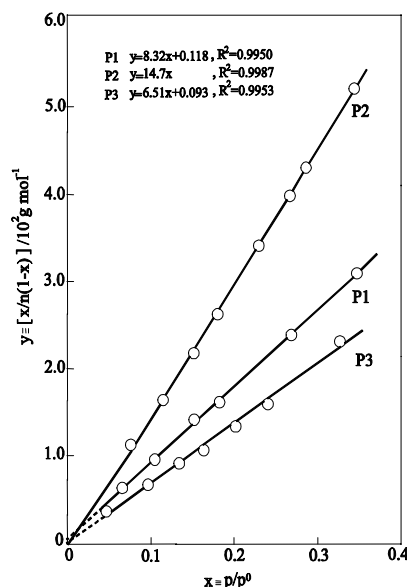


Fig. 3. Brunauer, Emmett, and Teller (BET) plots for the nitrogen adsorption on the alumina powders

vs. relative equilibrium pressure ($p/p^0 \equiv x$)³⁵. The dependence of the specific surface area for any test material on the standard multilayer thickness was obtained by using the last two equations and given as follows³⁶:

$$A/m^2 g^{-1} = 10^3 (V/cm^3 g^{-1}) \times (t/nm) \quad (4)$$

where $V/cm^3 g^{-1} = (34.6/cm^3 g^{-1}) \times (n/mol g^{-1})$ is the adsorption capacity as liquid nitrogen volume and $34.6 cm^3 g^{-1}$ is the molar volume of liquid nitrogen. The V-t plots were drawn for the powders by using experimental adsorption isotherms ($n-x$) and t -curve ($t-x$) at the corresponding $p/p^0 \equiv x$. These plots are given in Fig. 4. The specific surface areas of the powders were calculated from the last equation by using the slopes of the straight lines seen in Fig. 4 and given in Table-1.

Harkins-Jura method: An adsorption isotherm equation was derived based on a thermodynamic approach to the problem of physical adsorption and given as follows³⁷:

$$\log p/p^0 = B - C/v^2 \quad (5)$$

where $v/\text{cm}^3 \text{g}^{-1}$ is the adsorption capacity as gas volumes as standard temperature and pressure and B and C are constants. The surface area of an adsorbent is proportional to $C^{1/2}$ and the proportionality constant depending only on the nature of the adsorbate. If nitrogen at 77 K is the vapour adsorbed, then $C = 4.06$ and

$$A/\text{m}^2 \text{g}^{-1} = 4.06 C^{1/2} \quad (6)$$

gives the specific surface area. The plots of $\log(p/p^0)$ against $1/v^2$ for the alumina powder are straight lines as seen in Fig. 5. The surface area of every powder is calculated from the last equation by using the slope of the straight lines and is given in Table-1.

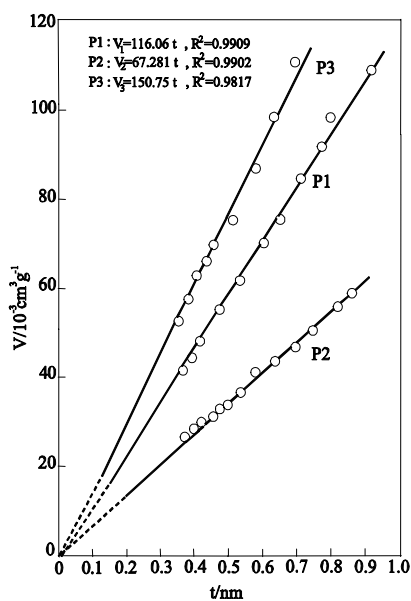


Fig. 4. Lippens and de Boer (LB) plots for the nitrogen adsorption on the alumina powders

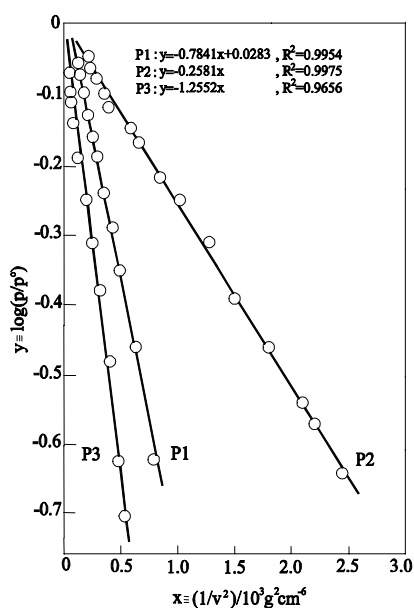


Fig. 5. Harkins and Jura (HJ) plots for the nitrogen adsorption on the alumina powders

Specific micro-mesopore volume and mesopore size distributions:

The adsorption capacity as liquid nitrogen volume obtained from the desorption isotherm at every x is taken as specific micro-mesopore volume (V) of filled pores in the alumina powders. The radii (r) of the mesopores assumed to be cylindrical were taken from literature for every x ³⁷. The mesopore size distribution as the dependence of specific micro-mesopore volume on

radius ($V-r$) was drawn for each powder and given in Fig. 6. As seen in Fig. 6, the mesopore size distributions depend on the preparation procedure of the precursors. It is well known that micropores and mesopores filled completely at a pre-determined $x = 0.96$ ($r = 25$ nm). Here, the total specific micro-mesopore volume is read from the mesopore size distribution curve at the corresponding $r = 25$ nm for each powders as seen in Fig. 6 and is given in Table-1.

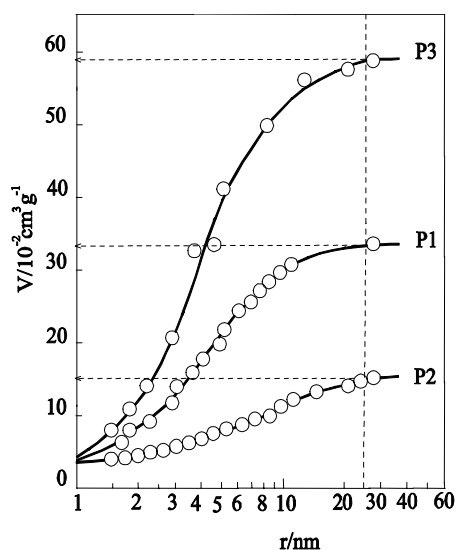


Fig. 6. Mesopore size distributions of the alumina powders and the determination of the specific micro- mesopore volumes

Conclusion

The morphology, surface area and pore volume of the powders depend on the preparation procedure of their precursors. While the powder obtained from first precursor (P1) precipitated heterogeneously contains shapeless particles, the powders obtained from second and third precursors (P2, P3) precipitated homogeneously contain agglomerates formed by spherical primer particle with the different sizes. The specific surface areas obtained from different methods are verified with each other. The powders are mainly mesopores materials and their micropores are less. The prepared powders can be used for the production of abrasive and membrane, adsorbent, chromatographic column support and catalyst.

ACKNOWLEDGEMENT

The authors thank the Scientific Research Project Council of Ankara University for supporting this work under the Project No: 2003-07.05.082.

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