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Determination of Pore Size Distribution by Transmission Electron Microscopy

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A simple method is suggested for preparing very thin films of alumina suitable for direct observation in a transmission electron microscope. The method consists of painting aluminum hydroxide gel on aluminum films, followed by dehydration at 500°C. The aluminum film is dissolved by amalgamation. Pore size distributions for γ- and η-alumina are measured directly and compared to those obtained by an adsorption–desorption technique.

INTRODUCTION

The surface area and the size distribution of the pores can be obtained indirectly from adsorption–desorption and from mercury porosimetry experiments. However, this information can be obtained directly by electron microscopy (*1*, *2*). In transmission electron microscopy (TEM) studies, a resolution of about 0.5 nm can be obtained, but the specimen has to be thinner than about 70 nm. A number of techniques for preparing very thin films are available. The material can be crushed and dispersed in a solvent and, after the larger particles have settled, a drop of the supernatant liquid evaporated on a carbon substrate film. Unfortunately, this procedure destroys the larger voids. Single-stage and double-stage replication can be used to examine surfaces but the resolution is not better than 5 nm. There also are difficulties in interpreting the micrographs. Several authors (*3–5*) have used the ultramicrotome to prepare thin films, but this procedure tends to modify the structure of the materials and also produces a great deal of debris. Faulkner *et al.* (*6*) used the ion-milling technique to prepare thin films of alumina.

A simple method is applied here to the aluminas to determine the size distribution of pores. The method consists of painting aluminum hydroxide gel onto thin aluminum foils and dehydrating them by heating. The dissolution of the aluminum by amalgamation produces a very thin film of alumina suitable for direct observation by TEM. The size distribution of the pores is determined directly from the electron micrographs, and from these measurements the surface area is calculated. The results provided by the TEM method are compared to those obtained by the nitrogen adsorption–desorption technique.

EXPERIMENTAL

Preparation of the aluminas. γ-Alumina and η-alumina were prepared by the thermal decomposition of boehmite and bayerite, respectively, at 500°C (*7*). The boehmite was obtained by adding aluminum nitrate solution to ammonium hydroxide solution. After the gel-like aluminum hydroxide precipitate was filtered and

washed, it was painted on thin aluminum foil precleaned with acetone and then pressed gently with a glass slide. The aluminum hydroxide, together with the aluminum foil, was dried at 120°C for 50 hr and then calcined for 24 hr at 500°C. The bayerite was obtained from the same solutions, but the pH was maintained above 9 by the addition of ammonium hydroxide. The precipitate was filtered and recontacted with water for 12 hr. After a second filtration it was painted on thin aluminum foil, dried for 72 hr at 120°C, and dehydrated to η-alumina by heating at 250°C for 16 hr and for an additional 24 hr at 500°C.

Preparation of the specimen for electron microscopy. The foils were cut into small parts using scissors and introduced into concentrated $HgCl_2$ solutions. After amalgamation, transparent parts of the alumina were picked up on grids, washed in distilled water for a few minutes, and picked up once again on fresh 100-mesh nickel grids. The specimens were heated at 300°C and 10^{-6} Torr for several minutes in an Edwards high vacuum coater and then stored under vacuum at room temperature to avoid contamination.

Evaluation of surface area. Five hundred pores were measured on each micrograph using a 7× magnifier to determine the size distribution of pores. Two measurements in diagonal directions were made on each pore in order to get the arithmetic mean radius, r. About 15% of the pores shown in the micrographs result from the collapse of two or three smaller pores. Frequently, however, each of the smaller pores retains enough of its initial cylindrical shape and surface area to be considered as an individual pore in the computations. After the size distribution was determined, the average pore radius, $\bar{r}$, was computed. The high contrast between the pore areas and the non-porous areas of the micrographs suggests that the pores are quasi-cylindrical in shape and have a length almost equal to the thickness of the film. The surface area per gram of alumina is given by

$$A = 2\pi\bar{r}nV,$$

where V is the specific volume (cubic

TABLE 1

Surface Areas and Size Distribution of Pores in Aluminas Dried at 500°C (Nitrogen Adsorption–Desorption)

	Data of MacIver *et al.* (7)		Present results	
	η-Al_2O_3	γ-Al_2O_3	η-Al_2O_3	γ-Al_2O_3
Surface area (m^2/g)	240	204	225	210
Average pore radius (nm)	2.16	2.94	2.60	2.93
Pore radius (nm)	Pore volume (%)			
<2	37.4		29.8	15.4
2–3	29.2	54.1	51.9	48.1
3–4	5.6	41.4	6.7	30.5
4–5	4.4	2.0	3.5	2.4
5–10	6.8	1.0	8.1	3.6
10–20	9.2	0.7		
>20	7.4	0.8		

TABLE 2

Surface Areas and Size Distribution of Pores in Aluminas Determined by TEM

	γ-Al_2O_3 (Figs. 1 and 2)		γ-Al_2O_3 (Figs. 3 and 4)		η-Al_2O_3 (Figs. 5 and 6)	
	500°C	600°C	500°C	600°C	500°C	600°C
Surface area, A (m^2/g)	269	210	278	211	299	234
Average pore radius, $\bar{r}$ (nm)	1.60	1.62	1.64	1.88	1.64	2.11
Specific volume, V (cm^3/g)	0.27	0.26	0.27	0.26	0.26	0.26
Pore radius, r^a (nm)	Pore volume (%)					
<1.0	7.7					
1.0–1.5	18.3	24.2	24.4	11.1	30.5	
1.5–2.0	66.6	65.6	62.9	72.1	50.6	25.5
2.0–2.5	7.4	8.7	11.8	11.9	18.6	48.0
2.5–3.0		1.5	0.9	3.5	0.3	20.0
3.0–3.5				1.4		6.5

[a] Collapsed pores are considered as formed by individual pores.

centimeters/gram) and n is the average number of pores per square centimeter.

SIZE DISTRIBUTION OF PORES

For comparison, the usual nitrogen adsorption techniques were also used to obtain the size distribution of the pores. The results obtained are tabulated in Table 1 where they are compared to results reported for aluminas prepared in the same way by MacIver *et al.* (*7*). Table 1 shows that γ-alumina has a rather uniform pore size with about 90% of the pore volume in the size range of 2–4-nm radius. η-Alumina, on the other hand, has 80% of the pore volume in the size range smaller than 3-nm radius, and the remainder is distributed among the larger pores.

The micrograph in Fig. 1 shows the microstructure of γ-alumina. Small particles with the retained morphology of the boehmite crystals, ranging from 50 to 120 nm in length and 20 to 50 nm in width, are visible.[1]

The size distribution, as well as the surface areas determined from the micrographs are presented in Table 2. The average pore radius of the alumina from Fig. 1 is 1.6 nm with 8% of the pores smaller than 1 nm (we ignore the pores which are too small to be detected by TEM). Reheating the alumina shown in Fig. 1 for 5 hr at 600°C leads to the microstructure shown in the micrograph of Fig. 2. The average pore radius is still 1.6 nm, but pores smaller than 1 nm no longer are observed. The surface area is reduced from 269 to 210 m^2/g because the number of pores per unit area is decreased.

Figures 1 and 2 show a chain array of pores in those particles which are thin (region 1, Fig. 2), two or three parallel chains in thicker particles (region 2, Fig. 2), and pores distributed more evenly in larger particles (region 3, Fig. 2). In the larger particles, the pores have a tendency to form six-neighbor close-packing

[1] Because the thickness of the specimen is not uniform, the focusing has to be taken into account in the interpretation of the micrographs. For instance, some of the white spots observed on the micrographs are the out-of-focus parts. Without a close examination, one can conclude wrongly that the morphology is different in the part for which the micrographs show crystallinity and in those parts for which they show large white spots.

arrangements. Figures 3 and 4 show another possible microstructure of γ-alumina. The micrograph of Fig. 4 represents the γ-alumina from Fig. 3 after heating at 600°C for 5 hr. Information about the size distribution as well as the surface areas are given in Table 2.

The size distribution of the pores in η-alumina (the corresponding micrographs are shown in Figs. 5 and 6) is broader than that of γ-alumina at the same temperature (see Table 2). Each pore on Fig. 5 is clearly defined. Pores larger than 3 nm no longer have a quasicircular section but are formed by the collapse of two or more pores; they have a distorted ellipsoidal shape. Pores smaller than 1 nm are not observed in η-alumina (Fig. 5), although they were observed in γ-alumina (Fig. 1). The micrograph in Fig. 6 represents the alumina of Fig. 5 heated at 600°C for 5 hr. Heating reduces the surface area, increases the sizes of the pores, and broadens the size distribution and the distribution of the number of neighbors around one pore. The distribution of the number of neighbors around one pore has, for η-alumina, a sharp peak (Fig. 7) for six neighbors, while for γ-alumina the pores are less ordered. It is this six-neighbor close packing of the pores which accounts for the high surface area in the aluminas.

DISCUSSION

The nitrogen adsorption–desorption technique assumes that the pores in the adsorbents are cylindrical in shape, open at either one or both ends, and involves tedious computation to obtain the size distribution. The TEM method is based on the direct observation of individual pores for the computation of both their size distribution and their surface area. Regarding the surface areas, the present results lead to values about 30% larger than those obtained by the nitrogen adsorption–desorption technique, probably because the adsorption–desorption measurements cannot accurately identify pores smaller than about 2 nm and because the length of pores assumed in the present computation is too large. The size distribution obtained by the present method is

FIG. 1. Transmission electron micrograph of γ-alumina, prepared by precipitation of aluminum nitrate with ammonium hydroxide and dehydration at 500°C for 24 hr. The micrograph shows particles with the retained morphology of the boehmite crystals.

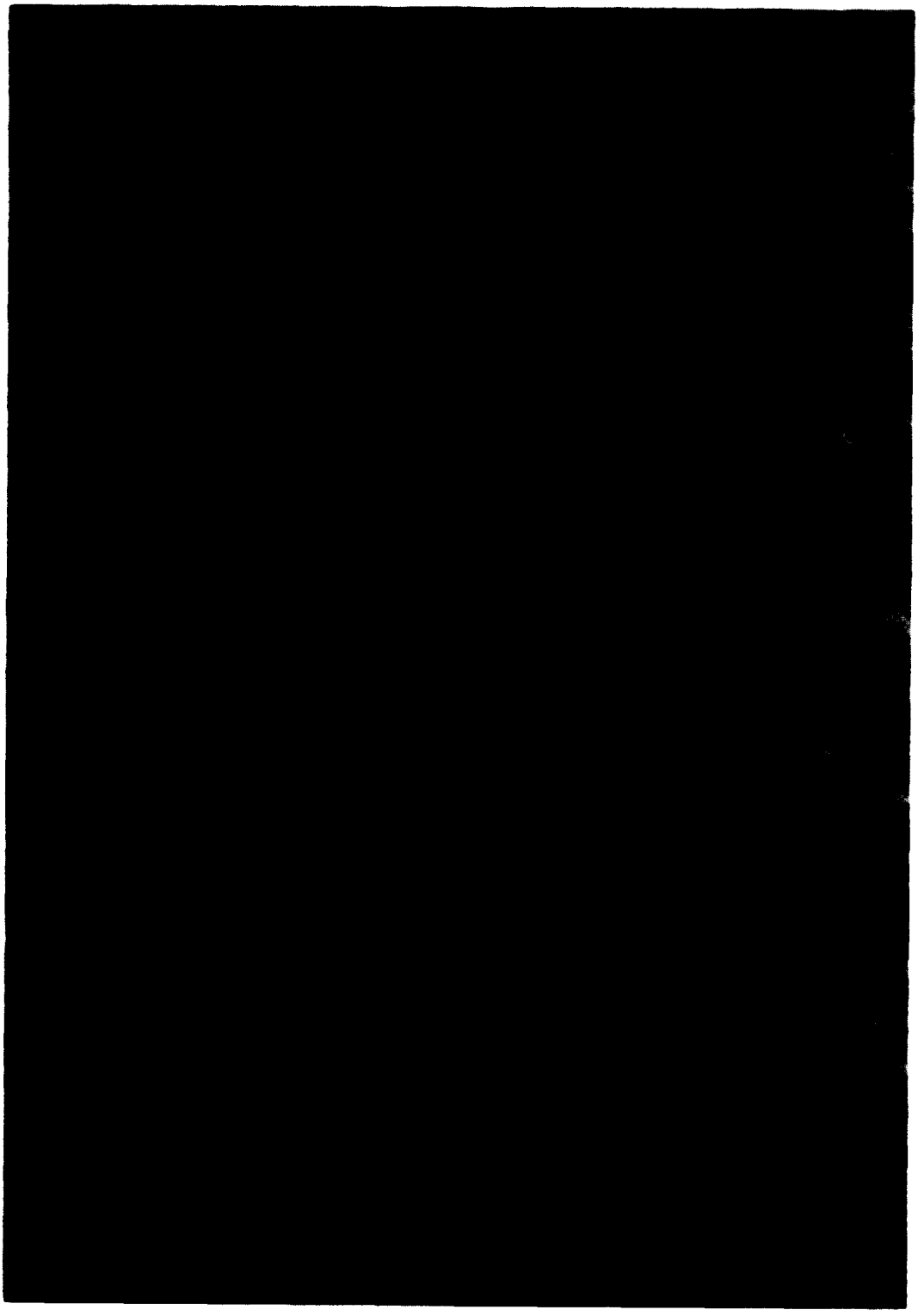
FIG. 2. Transmission electron micrograph of γ-alumina prepared by precipitation of aluminum nitrate with ammonium hydroxide, dehydration at 500°C for 24 hr and reheating for 5 hr at 600°C. The micrograph shows particles with the retained morphology of the boehmite crystals.

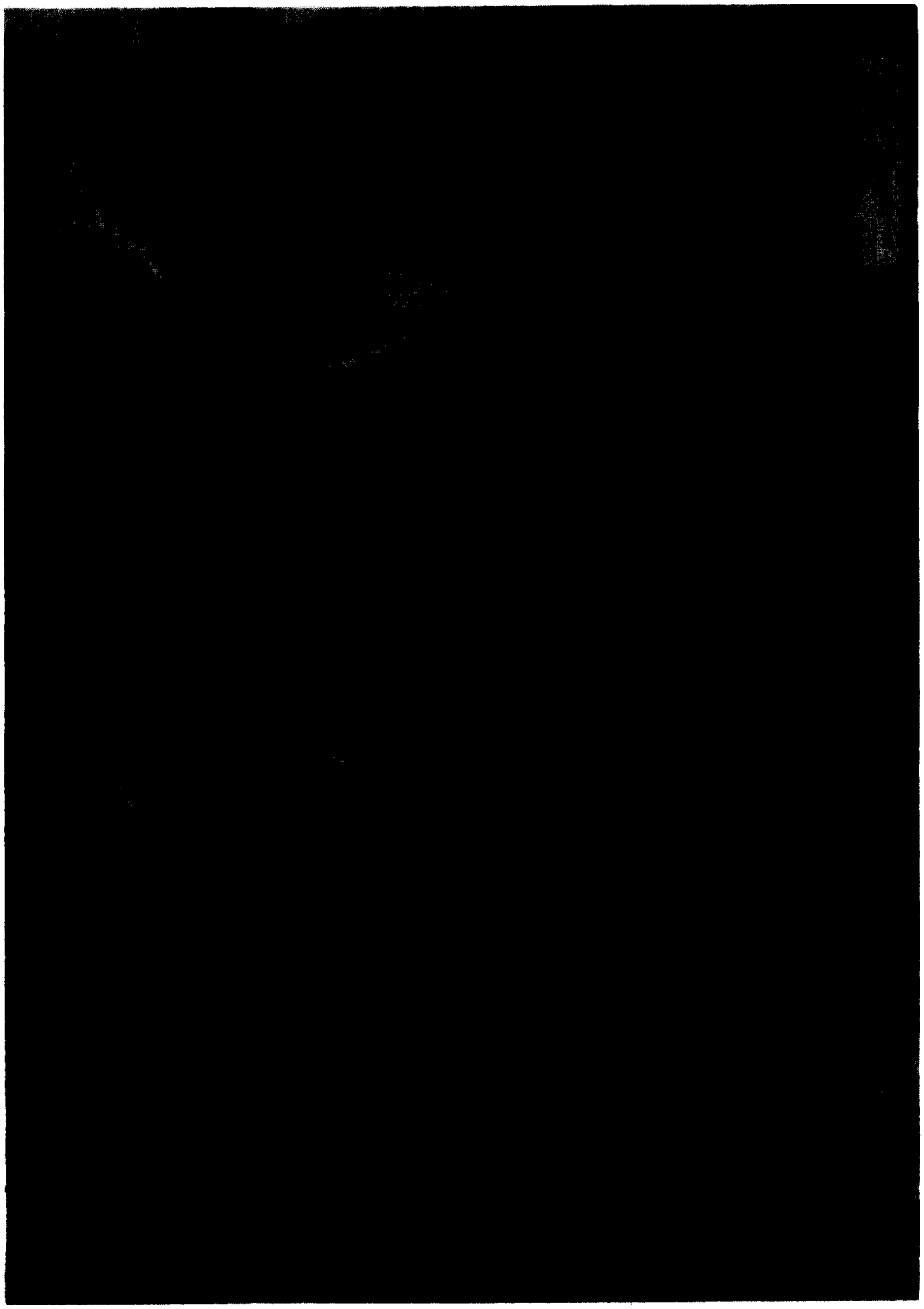
FIG. 3. Transmission electron micrograph of another microstructure of γ-alumina prepared by precipitation of aluminum nitrate with ammonium hydroxide and dehydration at 500°C for 24 hr.

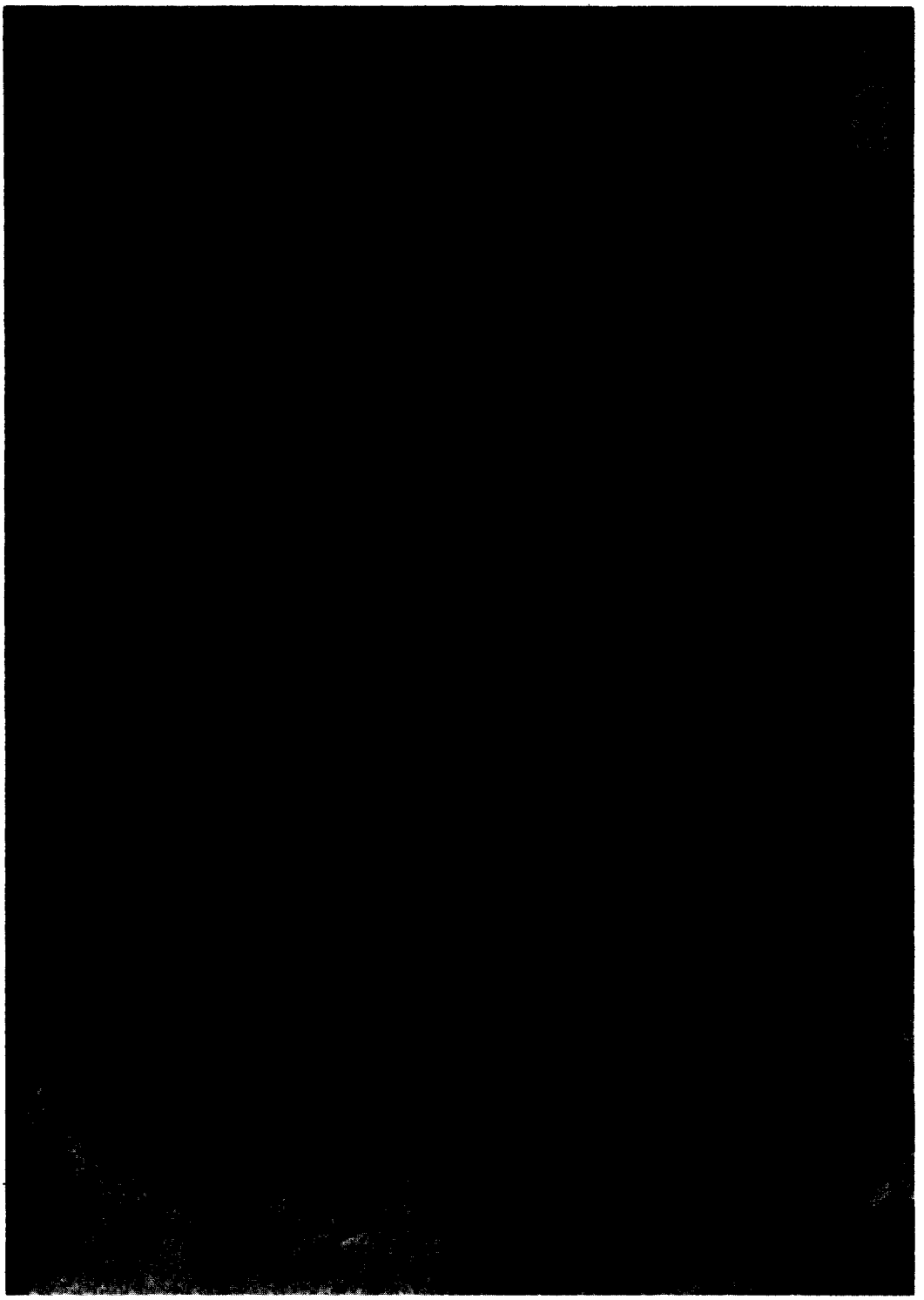
FIG. 4. Transmission electron micrograph of another microstructure of γ-alumina prepared by precipitation of aluminum nitrate with ammonium hydroxide, dehydration at 500°C for 24 hr, and reheating for 5 hr at 600°C.

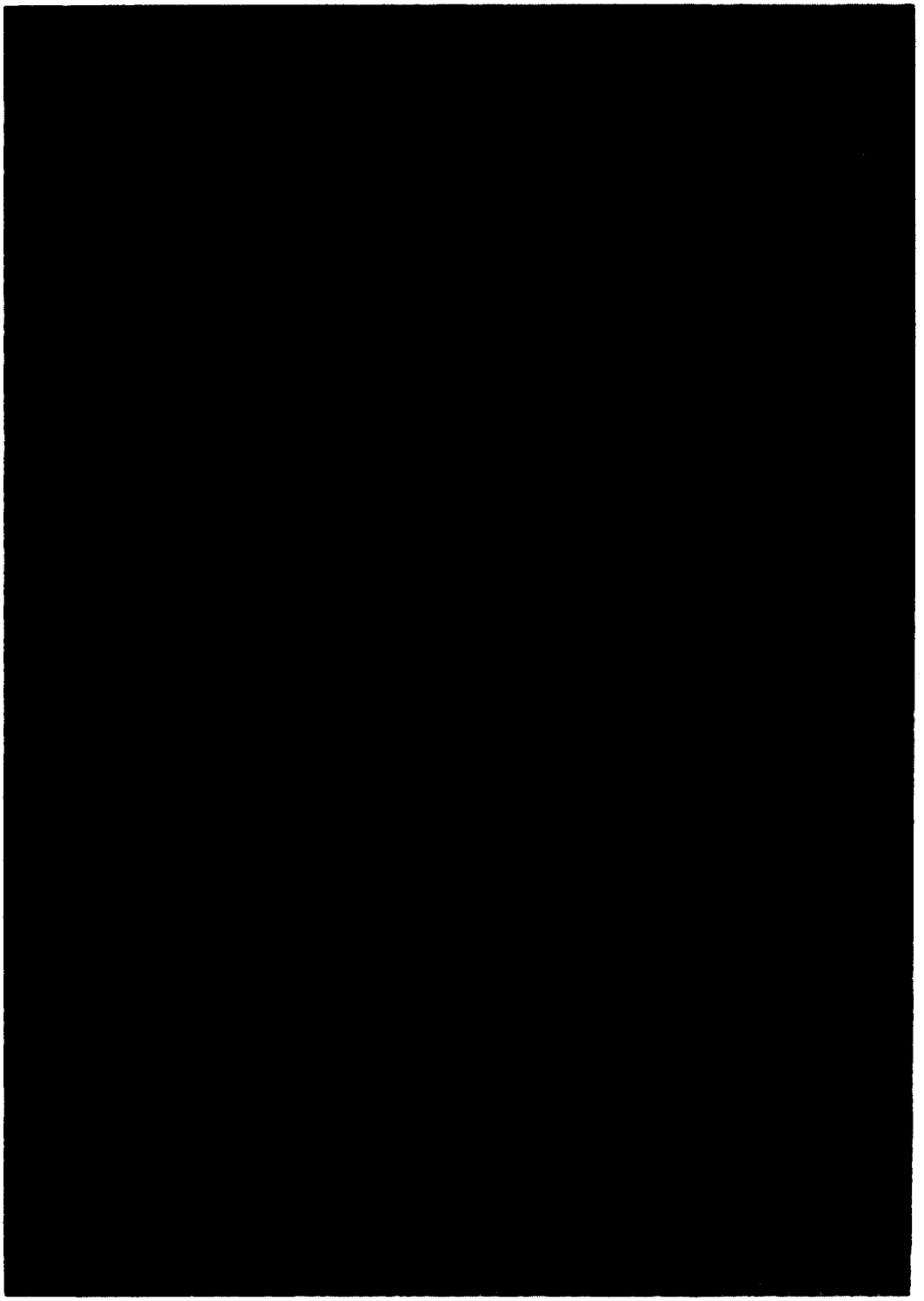
FIG. 5. Transmission electron micrograph of η-alumina prepared by precipitation of aluminum nitrate with ammonium hydroxide and dehydration for 24 hr at 500°C.

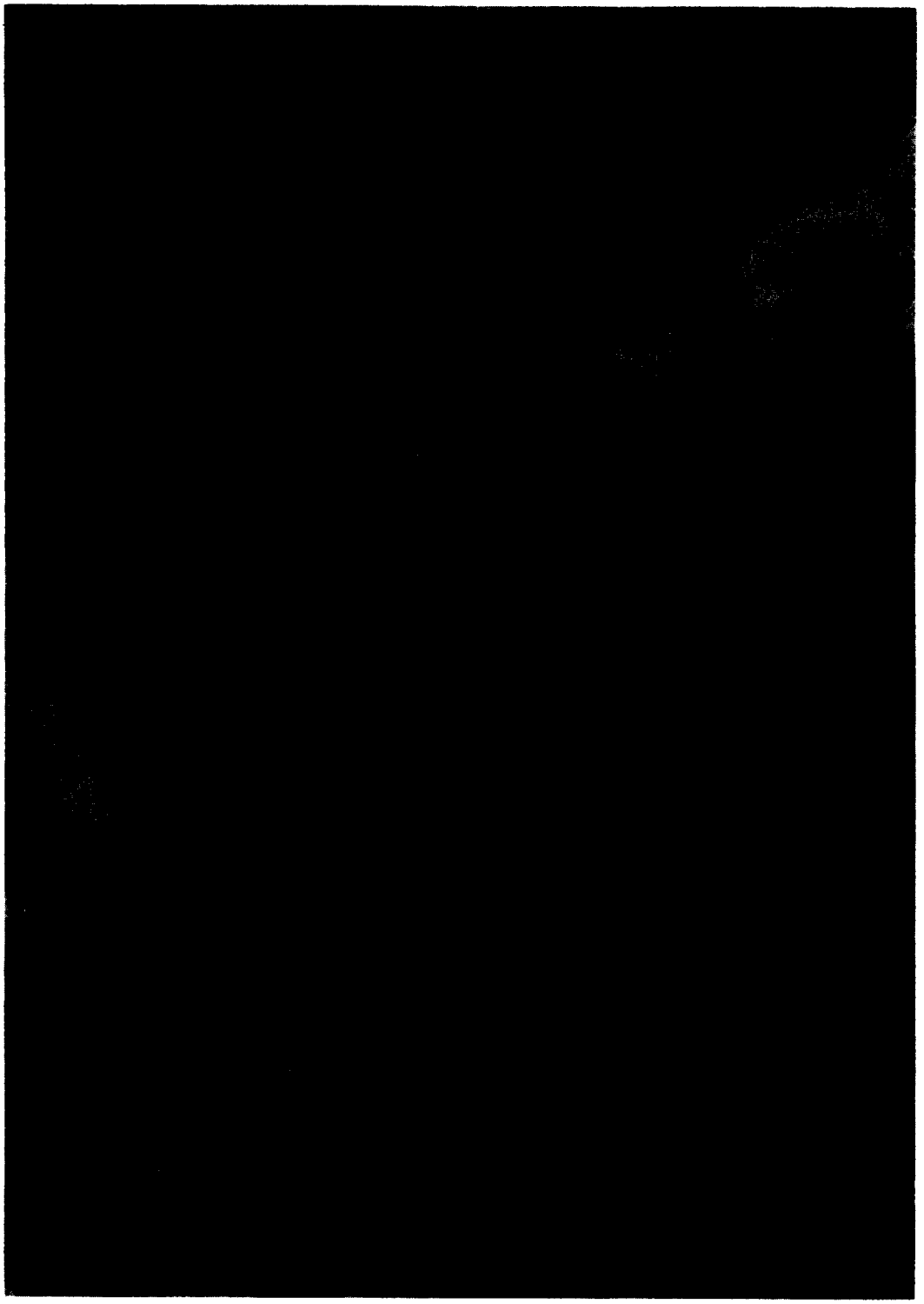
FIG. 6. Transmission electron micrograph of η-alumina prepared by precipitation of aluminum nitrate with ammonium hydroxide, dehydration at 500°C for 24 hr and reheating for 5 hr at 600°C.

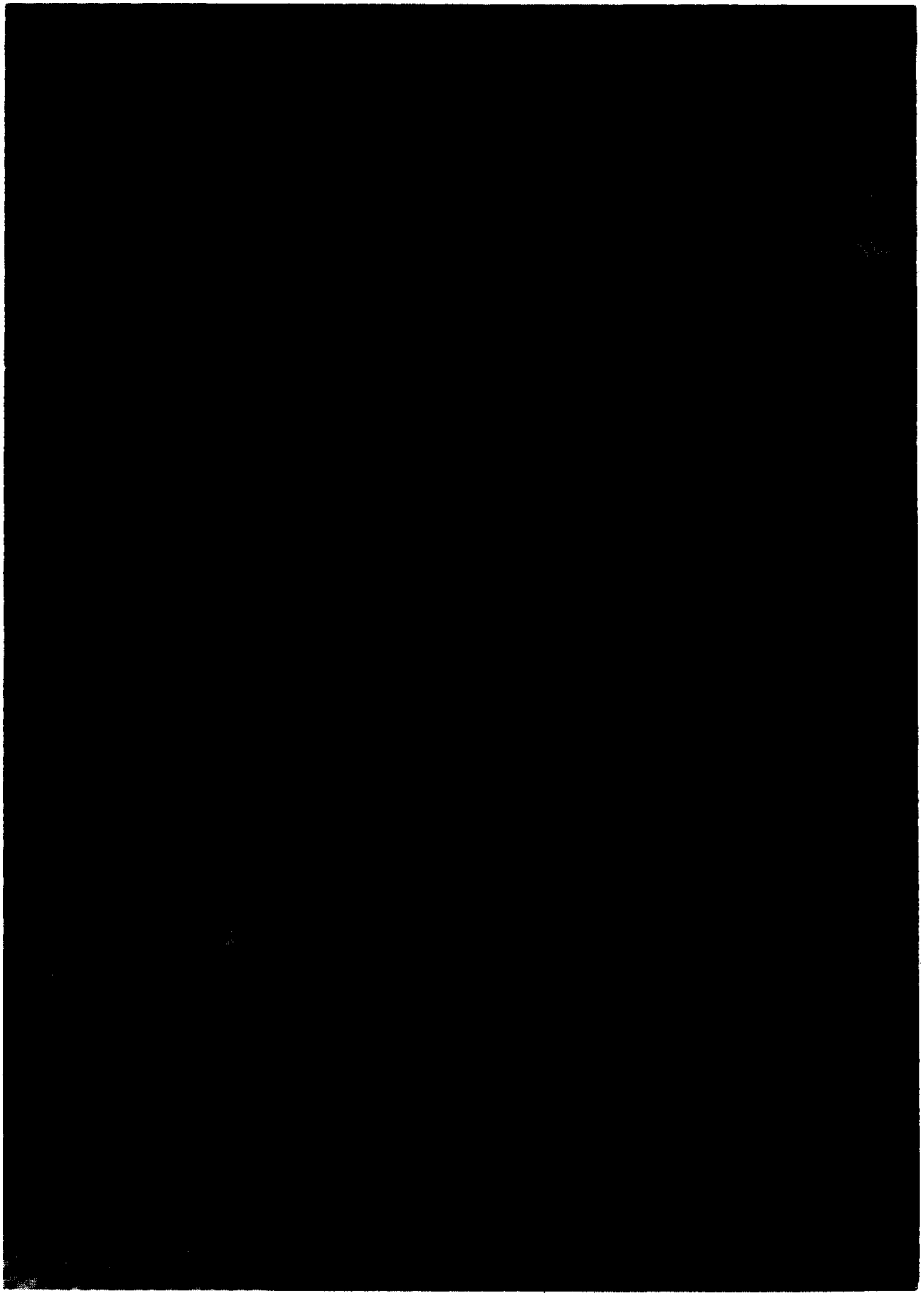












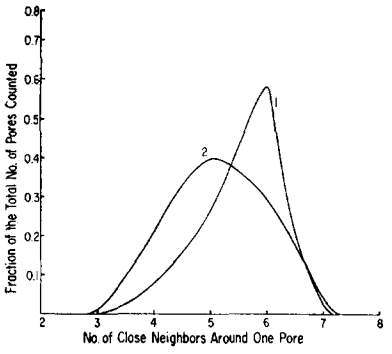


FIG. 7. Statistical distribution of the number of first neighboring pores around a pore. Curve 1, η-alumina dehydrated at 500°C; curve 2, same alumina as curve 1 after heating at 600°C for 5 hr.

more detailed than that provided by the adsorption–desorption technique and is displaced to smaller sizes.

The surface area reduction due to sintering at 600°C for 5 hr is different for η- and γ-alumina. For η-alumina the average number of pores per unit area is decreased while the average radius is increased from 1.6 to 2.1 nm. However, the fraction of the area occupied by the pores on the surface does not change. For γ-alumina, the average pore radius does not change significantly, but the fraction of the area occupied by the pores on the surface changes significantly. Possibly, the behavior of γ-alumina and η-alumina is affected by their water content and their acidity.

CONCLUSION

Transmission electron microscopy is an effective tool for the direct measurement of pore size distribution. A simple method is suggested here for the preparation of specimens suitable for direct observation in TEM. The method consists of (a) painting aluminum hydroxide gels on aluminum foils, (b) dehydrating them at elevated temperatures to obtain γ- or η-alumina, and (c) dissolution of the aluminum by amalgamation.

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