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Thermally Stabilized Transitional Alumina Prepared by Fume Pyrolysis of Boehmite Sols

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Alumina prepared by fume pyrolysis of sols consisting of fibrillar boehmite, 100 nm in length and 10 nm in diameter, was subjected to the thermal resistant tests. Even after calcination at 1473 K for 30 h, the alumina still consisted of fibrils and possessed a surface area as high as 50 m^2/g. This was ascribed to the suppression of the rate of phase transformation to α-alumina, caused by the fact that the alumina particles are of crude structures assembled by fibrils. © 1992 Academic Press, Inc.

INTRODUCTION

Because of industrial interest, techniques to prepare a thermally stabilized active alumina have been developed. Oudet *et al.* (*1*) reported that the thermal stabilization of transition alumina could be achieved by nucleating a cubic $LnAlO_3$ (Ln = La, Pr, Nd) on the surface of the alumina support. This was attributed to an inhibition of the structural transition to corundum by strong interaction between stable surface perovskite compounds ($LnAlO_3$) and the alumina. Doping the alumina support with foreign elements is another method for obtaining thermally stabilized active alumina. Amato *et al.* (*2*) developed techniques with which to suppress the enlargement of micropores in alumina by addition of BaO or SiO_2, leading to an inhibition of the sintering of the alumina support. Machida *et al.* (*3*) also used Ba^{2+} as dopant cations in alumina so as to form small $BaO \cdot 6Al_2O_3$ crystallites, which had the potential of resisting coagulation at high temperatures. Small $BaO \cdot 6Al_2O_3$ crystallites formed through a coprecipitation route using Ba and Al alkoxides exhibited high surface area, 10 m^2/g, even after the calcination at 1873 K (*4*). La^{2+} cations have also been employed as dopant ions in alumina supports to improve their thermal resistance (*5*). Matsuda *et al.* (*6*) reported that the layered compound of $La_2O_3 \cdot 11Al_2O_3$, similar to β-alumina in the crystallographic structure, had a high surface area, 37 m^2/g, after a calcination at 1473 K. Many other dopants such as zirconium (*7*), cerium (*8*), and rare earth metals (*9*) have been reported to bring about thermal stabilization of alumina supports.

In most of these works the stabilization of active alumina has been achieved by addition of foreign cations to produce thermally stable compounds on the alumina surface or to change the alumina into other materials such as $BaO \cdot 6Al_2O_3$ and $La_2O_3 \cdot 11Al_2O_3$. Catalysis by metals supported on these modified aluminas might be different from those on the original active alumina, since the catalysis by metals depends strongly on the support employed (*10*). Consequently, the thermal stabilization of active alumina is better achieved by alumina itself, i.e., without foreign additives. To evaluate the

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thermal resistance, the decrements in the specific surface area of aluminas, caused by sintering, have been measured after high-temperature treatments.

Since the sintering of active alumina has been widely accepted to progress simultaneously with the transition from a metastable phase to α-alumina at the contact area between particles (*11*), a key to suppressing the rate of sintering without additives is likely in the technique for preparing active aluminas with crude structures, where the contact area is small. The purpose of the present work is to prepare active aluminas composed of crude assemblies of alumina fibrils and to evaluate their thermal stabilization. In order to perform the purpose, the present alumina was prepared by fume pyrolysis of sol suspensions of fibrillar boehmite. The active aluminas thus prepared are small spheres roughly assembled by fibrils and actually have small contacting areas.

EXPERIMENTAL

The apparatus employed for a fume pyrolysis has been described elsewhere (*12*). Briefly, it consists of two parts; a reservoir for the sol suspensions, equipped with a supersonic vibrator (1.5 MHz) at the bottom to generate fumes into a reactor with flowing O_2 at the rate of 15 liter/min. Another part is the reactor made of quartz, equipped with three heaters at the top, middle, and bottom to give an appropriate temperature distribution. The reactor tube is 600 mm in length and 45 mm in diameter. Fumes generated were instantly burned out in the reactor to yield alumina spheres with about 1 μm of diameter, which were collected in the distilled water with a pH value of 7. These collected alumina spheres were dried and calcined at 773 K for 5 h, prior to the thermal resistant test at various temperatures. The fibrillar boehmite sols were prepared from aluminum isopropoxide (AIP) in the same manner as described in the previous paper (*13*). Alumina powders were also obtained from the fibrillar boehmite sol suspensions using ammonia water as a precipitant. The precipitates obtained were dried and calcined at 773 K to be supplied to the thermal tests, for comparison.

The thermal resistant tests were carried out in a high-quality alumina tube (30 mm diameter) with flowing dry air at the rate of 3 liter/min. The tests were performed at temperatures ranging from 773 to 1673 K for 5 h, and at 1473 K for 30 h, using about 2 g of alumina powders in the alumina tube. The thermal resistance was evaluated by measuring the change in the specific surface area of alumina after heating at high temperatures in flowing dry air. The surface areas were determined by BET measurements using N_2 at its liquid temperature. The change in the pore size distributions of the micropores in alumina was examined, in some cases, by the isothermal desorption of N_2 in adsorption/desorption measurements at 77 K (Shimazu Sorptomatic-1800).

Structural changes in alumina with heating time were monitored by X-ray diffraction (Rigakudenki Geigerflex), operated at 30 kV and 15 mA using a Ni filter for Cu$K\alpha$ irradiation. Measurements were all carried out at room temperature. Since the alumina particles were found to consist of alumina fibrils, the change in the morphology of the fibrils at high temperatures was studied by a transmission electron microscope (TEM, Hitachi, H-800), operated at an accelerating voltage of 200 kV and a magnification of $\times 10^5$. Alumina particles were dispersed in an organic resin and sliced into thin films, less than 100 nm thick, for TEM observation of cross sections of alumina spheres.

RESULTS

The apparatus used for fume pyrolysis is illustrated in Fig. 1 with temperature distributions inside the quartz tube, heated at 1123 K. Fumes were introduced into the tube by flowing O_2 at the rate of 15 liter/min, corresponding to linear velocity of 31 cm/s.

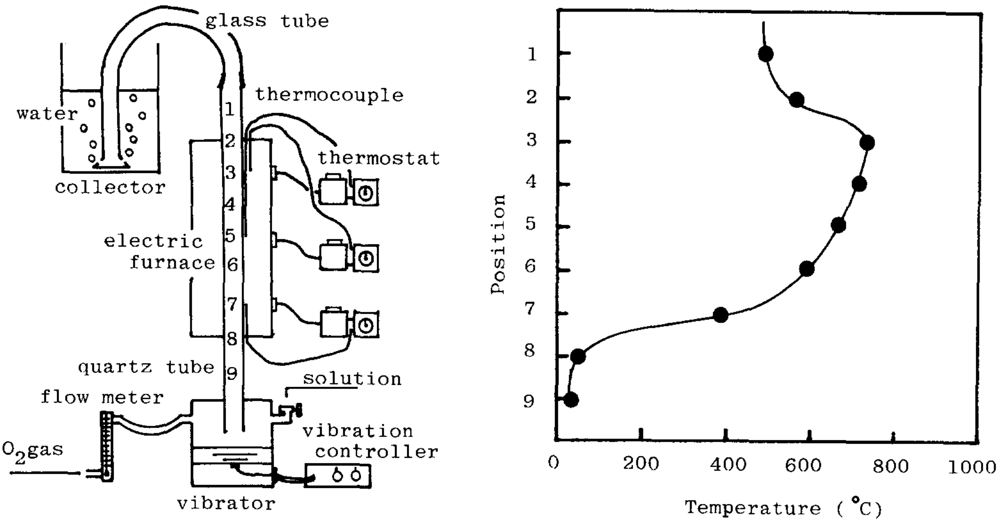

FIG. 1. Apparatus used for fume pyrolysis and the temperature distribution inside the reaction tube.

Changes in the specific surface area of alumina calcined for 5 h at high temperatures ranging from 773 to 1673 K in flowing dry air are shown in Fig. 2. The surface areas of both aluminas, prepared by fume pyrolysis and by precipitation, decreased extremely after heating at 1573 K for 5. However, there was a large difference in their surface areas after heating at 1473 K for 5 h. In Figs. 3a and 3b are given the changes in XRD spectra of aluminas by fume pyrolysis and by precipitation, respectively, with elevated calcination temperature. Pore size distributions of micropores in aluminas prepared by fume pyrolysis and successively calcined at 773, 1173, and 1473 K for 5 h, respectively, are illustrated in Fig. 4. The pore size distribution of alumina, prepared by precipitation and calcined at 773 K for 5 h, is also illustrated in Fig. 4.

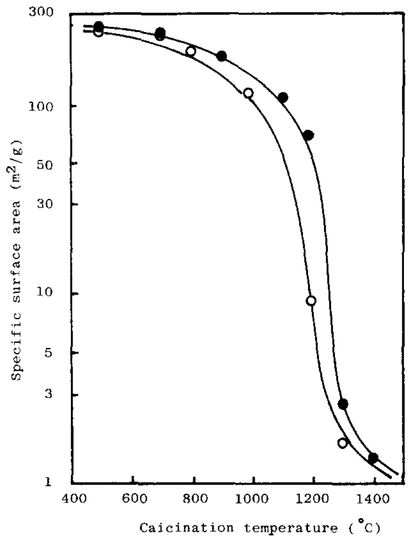

FIG. 2. Changes in the specific surface areas of alumina formed by fume pyrolysis (●) and by precipitation (○). Aluminas were calcined at each temperature for 5 h in flowing dry air.

TEM photographs of alumina spheres calcined at 773, 1173, 1473 and 1673 K for 5 h in flowing dry air are given in Figs. 5a to 5d, respectively, while TEM photographs of the cross section of these alumina spheres are shown in Figs. 6a to 6c. Although the alumina fibrils are still observed in the alumina spheres heated at 1173 K for 5 h, sintered and dense alumina particles are partially detected in the alumina heated at 1473 K for 5 h. A TEM photograph of fibrillar boehmite in the sol suspension employed for the fume pyrolysis is provided in Fig. 6d, for comparison.

Prolonged thermal resistant tests were

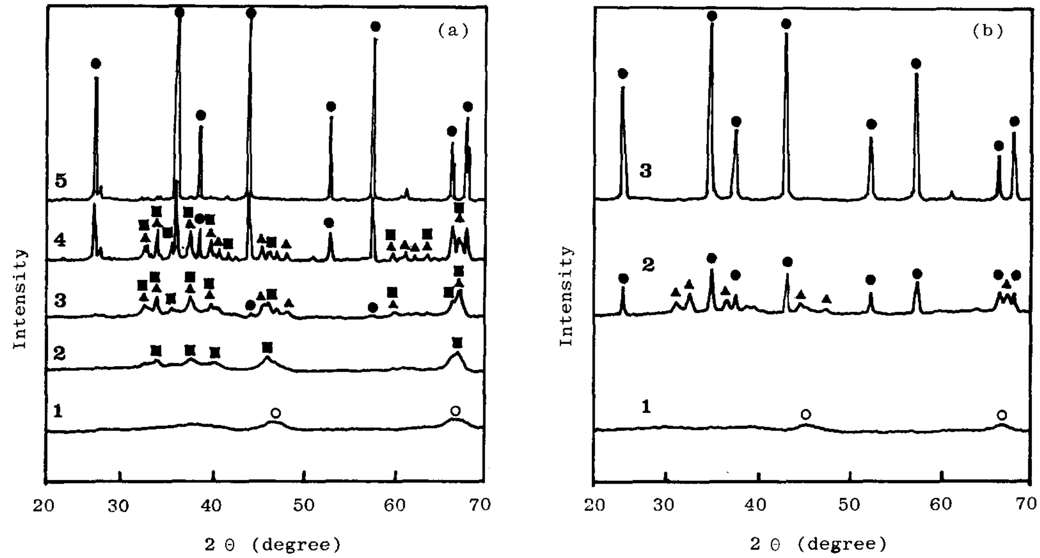

FIG. 3. Changes in XRD spectra of alumina by fume pyrolysis (a) and by precipitation (b) with the calcining temperature. (a) 1, 773 K; 2, 1373 K; 3, 1473 K; 4, 1573 K; 5, 1673 K; (b) 1, 773 K; 2, 1373 K; 3, 1473 K. (●) α-Al_2O_3; (○) γ-Al_2O_3; (■) δ-Al_2O_3; (▲) θ-Al_2O_3.

performed at 1473 K in flowing dry air using the alumina by fume pyrolysis, resulting in a rapid decrease of the specific surface area for the first 10 h of the heating. When heating the alumina for more than 15 h, the specific surface area is almost leveled off to be about 50 m^2/g, as seen in Fig. 7. Changes in the XRD spectra of the alumina with heating time at 1473 K are depicted in Fig. 8, where the rate of transition to α-alumina seems to be retarded.

DISCUSSION

The rate of phase transition of alumina from metastable states to α-alumina is well known to depend strongly upon the diffusion rate of impurity elements moving around alumina crystallites. Pt ions facilitate the rate of transition to α-alumina (*14*), while Ni ions inhibit the transformation to α-phase (*15*). Therefore, the thermal stabilization of alumina is affected by metal ions loaded on the alumina, employed as a support of metal catalysts. Nevertheless, it is still important to thermally stabilize the alumina by itself. In this study, alumina was prepared from AIP both by fume pyrolysis and by precipitation. One of the best methods for obtaining pure aluminas has been considered to be the use of AIP as a starting material (*16*). Consequently, no impurities that bring about problems are contained in the present aluminas.

As could be seen in Fig. 1, the temperatures inside the quartz tube are at most 873 K around the middle of the tube, even though it was heated outside at 1123 K. This is because of a heat release from the tube to the flowing gas, O_2. Since the linear velocity of the flowing gas was 31 cm/s, the residence time of fumes in the zone heated at 873 K was estimated to be less than 0.07 s. Organic compounds included in the fumes burned out instantly, when the fumes came into this zone. Since the burning occurs in an instant, the fibrillar sols in a droplet of fumes could not coagulate densely, yielding small spheres of crude assemblies consisting of alumina fibrils. After calcining the resulting alumina at 773 K for 5 h, the crude structures still remained, as evidenced in Figs. 5a and 6a. In these crude structures, the contacting

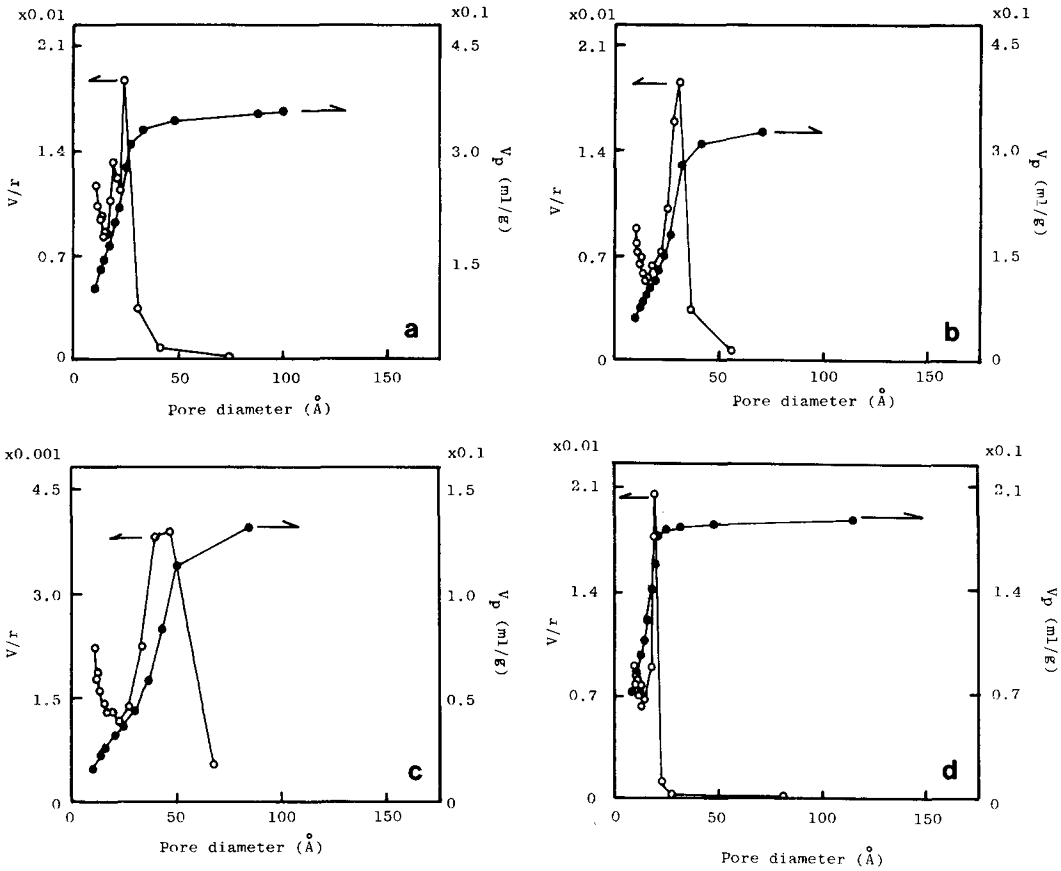

FIG. 4. Pore size distribution of alumina by fume pyrolysis; after calcination at 773 K (a), 1173 K (b), and 1473 K (c) for 5 h, respectively. (d) represents the pore size distribution of alumina prepared by precipitation and successively calcined at 773 K for 5 h.

areas between fibrils were less than those in the alumina prepared by a precipitation route.

The decreases in the specific surface areas of both aluminas by fume pyrolysis and precipitation are shown in Fig. 2 against the heating temperature. There was a great difference between the surface areas of the two aluminas calcined at 1473 K for 5 h. A significant decrease in the surface areas for both aluminas calcined at 1573 K for 5 h was attributed to the growth of corundum crystallites, as evidenced by XRD spectra shown in Figs. 3a and 3b. In the alumina prepared by precipitation, the formation of α-alumina was detected when calcined at 1373 K for 5 h. However, in the alumina prepared by fume pyrolysis, almost no peaks assigned to α-alumina were observed in the XRD spectrum even after heating at 1473 K for 5 h. This means that the transition to corundum was retarded in the alumina prepared by a fume pyrolysis, since the transition temperature is reported to be 1373 K (*17*). As the surface area of the alumina decreased, the mean pore size of its micropores gradually increased from 25 to 45 Å and, instantaneously, the pore volume decreased from 0.34 to 0.13 ml/g (see Fig. 4). The pore size distribution of micropores in the alumina by precipitation is also given in Fig. 4, for comparison. The mean pore sizes of both aluminas heated at 773 K for 5 h are almost the same, about 25 Å. The pore

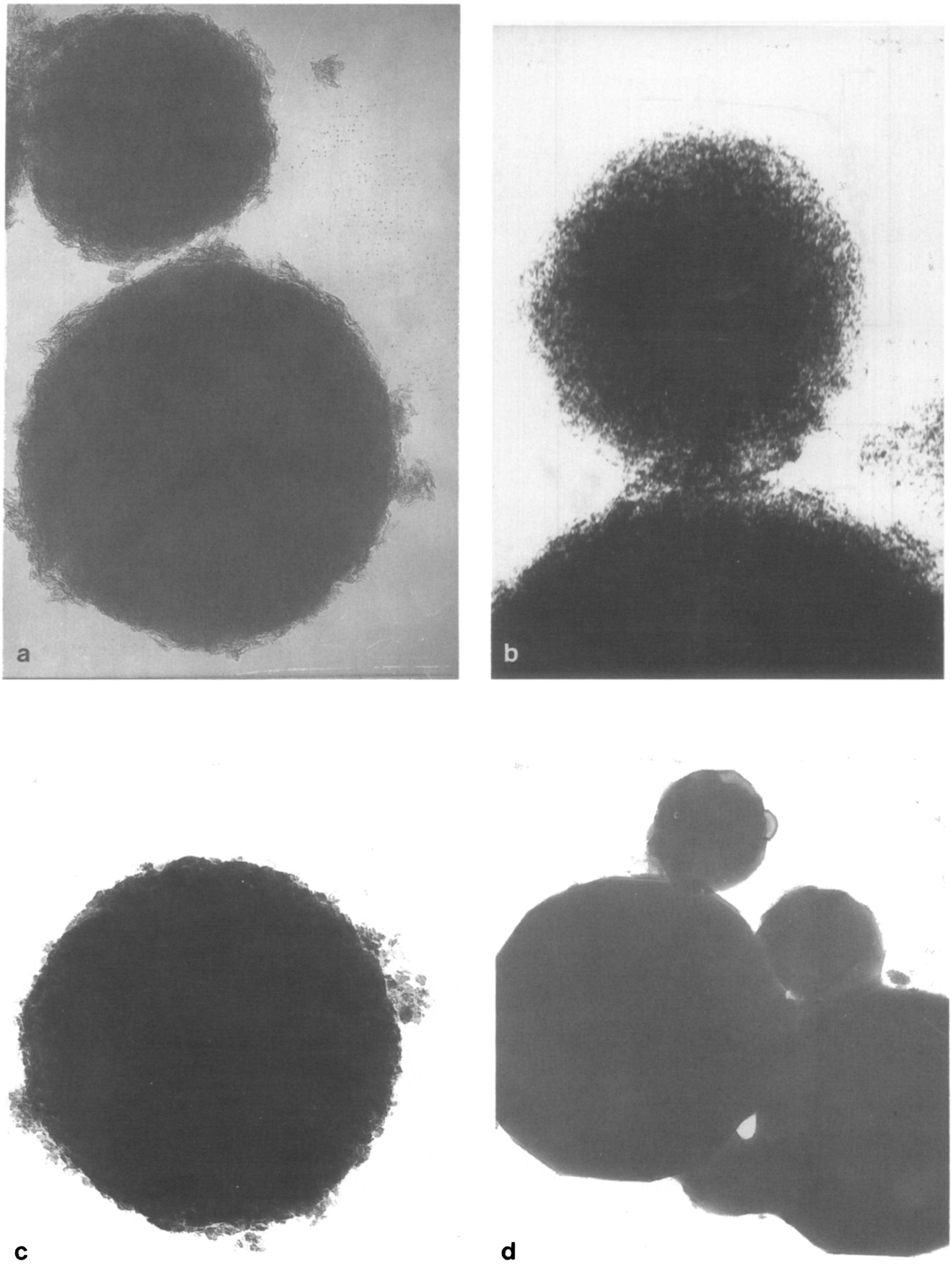

FIG. 5. TEM photographs of alumina by fume pyrolysis; after calcination at 773 K (a), 1173 K (b), 1473 K (c), and 1673 K (d) for 5 h, respectively.

volume of the alumina from fume pyrolysis was 1.5 times larger than that of the alumina from precipitation. This indicates that the alumina by fume pyrolysis was composed of crude assemblies of alumina fibrils so as to have a large pore volume. In other words, the contacting area between fibrils in the alumina by fume pyrolysis was much smaller than that in the precipitated alumina.

Aluminas prepared by fume pyrolysis and subsequently heated at 773 K for 5 h are spheres with about 1 μm diameter, as shown in Fig. 5a. Fibrils are obviously seen at the fringes of spheres shown in Figs. 5a and 5b. As seen in Figs. 6a and 6b, the fibrillar structures are also observed inside the alumina spheres even after heating at 1173 K for 5 h. By heating the alumina at 1473 K for 5 h the spheres became rather rigid and no fibrils could even be detected at their fringes (see Fig. 5c). Sintered and dense particles, marked by arrows in Fig. 6c, were partially produced inside the alumina spheres heated at 1473 K for 5 h, although fibrils were still observed predominantly. Thus, crude structures consisting of alumina fibrils remained in the alumina prepared by fume pyrolysis even when calcined at 1473 K for 5 h, resulting in a large surface area of 70 m^2/g (see Fig. 2).

The decrease in the specific surface area of fumed alumina calcined at 1473 K for a prolonged time is given in Fig. 7a, and that of alumina prepared by precipitation is given in Fig. 7b, for comparison. Although the specific surface areas of both aluminas calcined at 773 K for 5 h are almost the same, about 270 m^2/g, the rates of decrease in their surface areas are significantly different. The alumina by precipitation lost more than 95% of the surface area when calcined at 1473 for 5 h, while the alumina prepared by fume pyrolysis still exhibited a high surface area of 70 m^2/g when heated at the same temperature for 5 h. The alumina prepared by fume pyrolysis possessed high thermal resistance so that the reduction in its surface area leveled off after heating at 1473 K for 15 h, leading to a constant value around 50 m^2/g after prolonged heating at 1473 K. This high thermal stabilization of the alumina is associated with the retardation of phase transition to α-alumina. Figure 8 shows a negligibly small amount of α-alumina even after heating the fumed alumina at 1473 for as long as 30 h. Most of the alumina converted to the crystallographic δ and θ structures when heated at 1473 K.

The high thermal stabilization and the associated retardation of phase transition in the present alumina seems to be ascribed to the crude structures of the alumina prepared by fume pyrolysis using the sols of fibrillar boehmite. It results in a small contact area between the constituent fibrils in the fired alumina. According to theory (*18*), the sintering, hence the phase transition to α-alumina, first takes place at the contact area between particles. Mutual diffusions of ions through the contact area follow as the crystallites grow.

Thus, the small contact areas between fibrils, in the present alumina, are of crucial importance to establish the thermal stabilization of alumina. The reduction rate of surface area during sintering is often describes as $dS/S_0 = -K \cdot (B \cdot t)^{m/N}$, where dS/S_0 is the normalized reduction of the specific surface area, t is the isothermal sintering time, B is a constant depending on the material property, particle size, and temperature, and K, m, and N are the constants for a given set of conditions dictated by the controlling mechanism (*19*). The controlling mechanism of sintering could be discussed by estimating the magnitudes of the inverse exponential factor, N/m, around 1.1 for viscous or plastic flow mechanism, around 2.7 for volume diffusion mechanism, and around 3.5 for surface diffusion mechanism, respectively (*19*). Although the above equation assumes the sintering of monosized spheres, we used it to analyze the data in Fig. 7 in an attempt to discuss the controlling mechanism for sintering of the present alumina. In order to obtain S_0, the specific surface area of the alumina immediately after the intro-

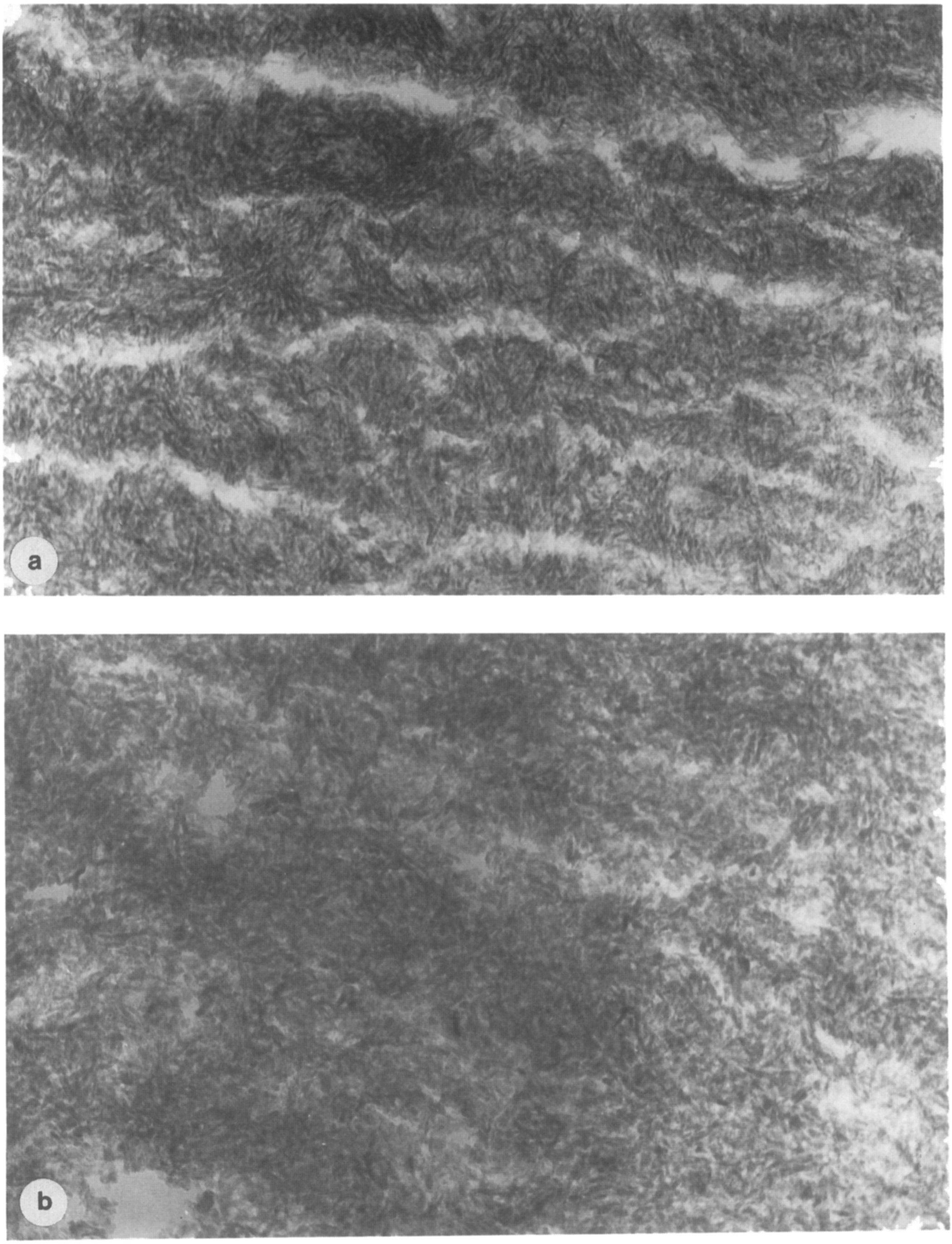

FIG. 6. TEM photographs of cross sections of alumina spheres; after calcination at 773 K (a), 1173 K (b), and 1473 K (c) for 5 h, respectively. (d) is the fibrillar boehmite in the sol suspensions employed for fume pyrolysis.

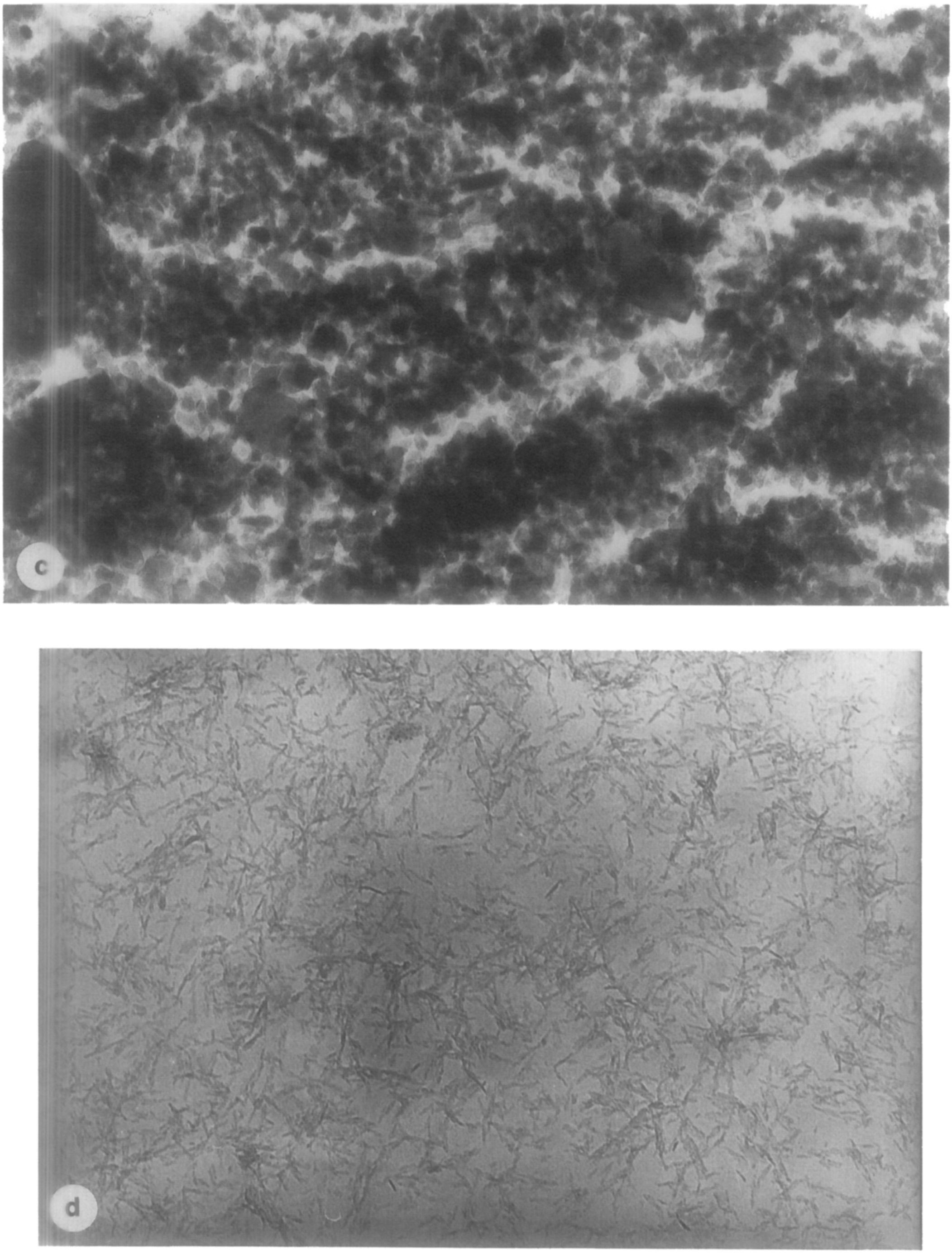

FIG. 6—*Continued*

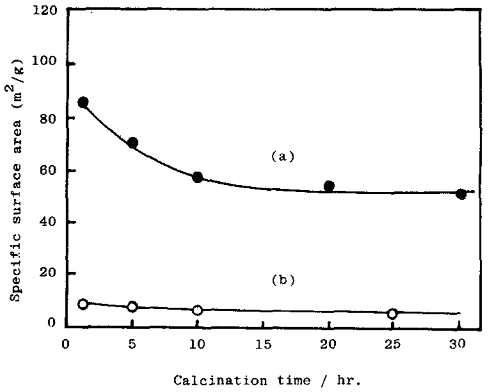

FIG. 7. Surface area reduction of alumina with a prolonged calcination at 1473 K in flowing dry air. (a) Alumina prepared by fume pyrolysis and (b) alumina prepared by precipitation.

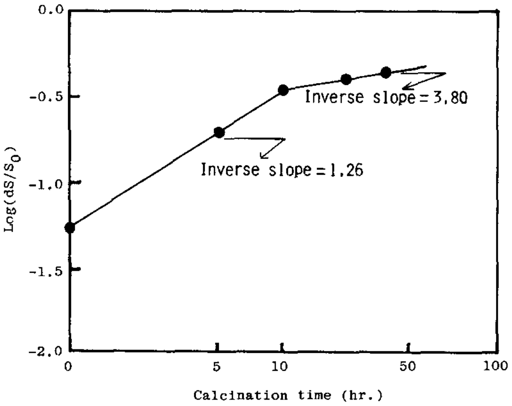

FIG. 9. Normalized reduction of surface area data employed.

duction into the heating tube at 1473 K, the curve in Fig. 7 was extrapolated to time zero. S_0 thus estimated was 90 m^2/g and $\log(dS/S_0)$ against t was plotted, as shown in Fig. 9. The curve in Fig. 9 suggests two slopes; at the first stage of sintering the inverse slope is 1.2, indicating the viscous or plastic flow mechanism and at the other stage the inverse slope is 3.8, corresponding to that of surface diffusion mechanism. From these results, it might be possible to say that in the first 10 h of sintering, surface melting takes place at the contact area between tiny fibrils to diminish the micropores. Then, surface diffusion occurs, starting at the contact areas and growing small corundum crystallites in the vicinity of surface fibrils. Regardless, corundum layers formed over the surface of fibrils will retard the rate of crystalline growth of corundum into the bulk, probably because the surface to volume ratio of fibrils is so large that the surface compound (corundum) might control the properties of fibrils. Corundum is thermally more stable than the active alumina. This is the reason why small amounts of corundum could be detected in XRD spectra, shown in Fig. 8, even after the calcination at 1473 K for as long as 30 h. How the surface corundum layers inhibit the crystalline growth of corundum into the bulk of fibrils is still ambiguous.

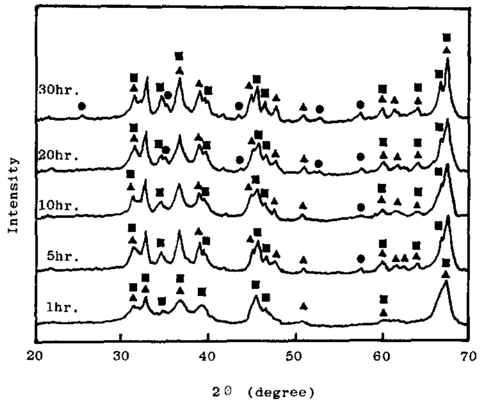

FIG. 8. Change in XRD spectra of alumina by fume pyrolysis during a prolonged calcination at 1473 K. (●) α-Al_2O_3; (■) δ-Al_2O_3; (▲) θ-Al_2O_3.

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REFERENCES

1. Oudet, F., Courtine, P., and Vejux, A., *J. Catal.* **114,** 112 (1988).
2. Amato, I., Martorana, D., and Silengo, B., *in* "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 187, Plenum Press, New York/London, 1975.
3. Machida, M., Eguchi, K., and Arai, H., *J. Catal.* **103,** 385 (1987).

4. Machida, M., Eguchi, K., and Arai, H., *Chem. Lett.*, 1993 (1986).
5. Schaper, H., Doesburg, E. B. M., and Papee, D., *J. Appl. Catal.* **7,** 211 (1983).
6. Matsuda, S., Kato, A., Mizumoto, M., and Yamashita, H., "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 4, p. 879. Dechema, Frankfurt-am-Main, 1984.
7. Bettman, M. and Yao, H. C., *in* "Sintering and Catalysis", G. C. Kuczynski, Ed.), p. 165. Plenum Press, New York/London, 1975.
8. Gaugin, R., Graulier, M., and Papee, D., *Adv. Chem. Ser.* **143,** 147 (1975).
9. Oudet, F., Bordes, E., Courtine, P., Maxant, G., Lambert, C., and Guerlet, J. P., *in* "Studies in Surface Science and Catalysis" (A. Frennet, Ed.), Vol. 30, p. 313. Elsevier, Amsterdam, 1987.
10. Tauster, S. J., Fung, S. C., and Carten, R. L., *J. Am. Chem. Soc.* **100,** 170 (1980); Tauster, S. J., and Fung, S. C., *J. Catal.* **55,** 29 (1978).
11. German, R. M., and Munir, Z. A., *in* "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 249. Plenum Press, New York/London, 1975.
12. Ogawa, T., Yamada, S., Miki, T., Tsuiki, H., Kakuta, N., Ueno, A., Suzuki, Y., Koyama, K., Noguchi, S., and Yamada, M., *Bull. Chem. Soc. Jpn.* **62,** 1844 (1989).
13. Ishiguro, K., Ishikawa, T., Kakuta, N., Ueno, A., Mitarai, M., and Kamo, T., *J. Catal.* **123,** 523 (1990).
14. Kozolov, N. S., Lazarev, M. Y., Mostovaya, L. Y., and Stremok, I. P., *J. Kinet. Catal.* **14,** 1130 (1973).
15. Young, D. J., Udaja, P., and Trimm, D. L., *in* "Catalyst Deactivation" (B. Delmon, Ed.), p. 331. Elsevier, Amsterdam, 1980.
16. Yoldas, B. E., *Am. Ceram. Soc. Bull.* **54,** 286, 289 (1975).
17. Gitzen, W. H., "Alumina as a Ceramic Material." The American Ceramic Society, Columbus, OH, 1970.
18. Exner, H. E., and Petzow, G., *in* "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 279. Plenum Press, New York/London, 1975.
19. Rockland, J. G. R., Acta Metall. **14,** 1273 (1967); **15,** 277 (1967); German, R. M., and Munir, Z. A., *in* "Sintering and Catalysis" (G. C. Kuczynski, Ed.), p. 259. Plenum Press, New York/London, 1975; Williams, A., Butler, G. A., and Hammonds, J., *J. Catal.* **24,** 352 (1974); Fynn, P. C., and Wanke, S. E., *J. Catal.* **34,** 400 (1974).