JOURNAL OF CATALYSIS 145, 450–455 (1994)

Stabilized Aluminum Oxide Prepared by Heat Treatment of Aluminum Hydroxide Sols in a Carbon Matrix

Z. Jaworska-Galas,* W. Mista,* J. Wrzyszcz,* M. Zawadzki,* and J. Machnikowski†

*Department of Catalysis, W. Trzebiatowski Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 937, 50-950 Wrocław, Poland; and †Institute of Chemistry and Technology of Petroleum and Coal, Technical University of Wrocław, 50-344 Wrocław, Poland

Received January 21, 1993; revised May 19, 1993

Transition aluminum oxides with increased thermal stability were obtained by placing dispersed aluminum hydroxides in a carbon matrix, their particles being respectively quasispheroidal and fibrous, and holding at a temperature of 2000 K in an argon atmosphere for 30 min; afterwards, the carbon phase was burned in air at 1073 K. Subsequent calcination in air showed that the specimens of Al_2O_3 still consisted of the fibrous and quasi-spheroidal particles and that their increased specific surface was conserved. Simultaneously, a delay in the phase transitions to corundum and stabilization of the δ-Al_2O_3 phase at 1473 K was observed. © 1994 Academic Press, Inc.

INTRODUCTION

Transition aluminas with increased thermal resistance for sintering are interesting materials for use as catalyst supports in high-temperature processes. They can be used in catalytic systems for gas cleaning and emission control, steam reforming and others. The phase transition of γ-Al_2O_3 to α-Al_2O_3, occurring at ca. 1275 K and leading to drastic decrease in specific surface area, can be slowed down by adding alkaline earths or rare earths, as well as SiO_2, ZrO_2, or TiO_2. This stabilization arises from the formation of β-Al_2O_3, which has a layered structure of the plumbite type, or from physical separation of alumina particles, which makes interface reactions more difficult (1–6).

In the 1950s, a phase with high thermal stability which was similar to δ-Al_2O_3 was detected in the reaction products of corundum with aluminum carbide or nitride (7–9). The carriers obtained in this way did not contain foreign ions and their stabilization arose from the formation of solid solutions of the Al_2OC–AlN type, which prevented recrystallization (10, 11). Formation of a monolayer of AlON on the Al_2O_3 surface is also possible, giving similar results (12).

The aim of this work was to investigate the properties of aluminum oxides obtained by calcination of boehmite which was pretreated in a carbon matrix at 2000 K in an argon atmosphere. The investigated materials were sols of spheroidal and fibrous aluminum oxide. It is known that the morphology of particles may influence their susceptibility to sintering (13).

EXPERIMENTAL

The raw material for the preparation of specimens was aluminum hydroxide obtained by hydrolysis of small pieces of solid aluminum tri-*iso*-propoxide introduced into excess of boiling water under vigorous stirring. A sol of quasi-spheroidal particles was then obtained by peptization of the 5 wt% dispersion of aluminum hydroxide by 1.5 wt% nitric acid (molar ratio was 0.05 mol HNO_3/1 mol Al_2O_3) at 360 K for 20 h. The sol of fibrous particles was obtained under hydrothermal conditions: a 5 wt% dispersion of aluminum hydroxide was peptized with 1 mol HNO_3/1 mol Al_2O_3 in an autoclave at 450 K (pressure 1.0 MPa) for 6 h.

The sols of aluminum hydroxide so obtained were mixed with a 30 wt% aqueous solution of saccharose (the ratio was 1 g Al_2O_3/9 g $C_{12}H_{22}O_{11}$). Water was then evaporated and the residue was carbonized at 800 K in a retort under vacuum.

The samples were heated in an electric resistance graphite furnace. The heating rate was 10 K/min, and the heat treatment was carried out in a steam of argon (nitrogen content lower than 0.01 vol%). The final temperature was 2000 K and the time at the final temperature was 30 min (14). The carbon matrix was burned by heating the samples in air at 1073 K for 12 h. The white powders obtained were calcined again in air for 3 h at, respectively, 1273, 1473, 1573, and 1623 K.

For comparison purposes, the samples of dried alumina sols were calcined at the same temperatures.

The phase composition and mean crystallite sizes were determined using X-ray diffraction (DRON-3 diffractometer using Cu $K\alpha$ radiation and Ni filter).

0021-9517/94 $6.00

TABLE 1

Specific Surface Area S_{BET} (in $m^2\ g^{-1}$) of the Samples with and without Carbon Matrix

	Temperature and time of calcination									
	1073 K/12 h		1273 K/3 h		1473 K/3 h		1573 K/3 h		1623 K/3h	
Sample	With matrix	Without matrix	With matrix	Without matrix	With matrix	Without matrix	With matrix	Without matrix	With matrix	Without matrix
Spheroidal precursor	120	125	135	89	65	11	24	8	8.6	4.5
Fibrous precursor	72	194	59	123	40	8	35	7	18	6

Morphological changes of the sample particles were observed using a transmission electron microscope (TESLA BS 500).

The specific surface area was determined using a Perkin–Elmer 212 D sorptometer. Nitrogen was used as the adsorbate and the specific surface area was calculated using the BET method.

RESULTS AND DISCUSSION

The values of specific surface areas of the samples under investigation are given in Table 1. In this table, data are given for materials obtained from both spheroidal and fibrous precursors. The materials were calcined at the temperatures indicated.

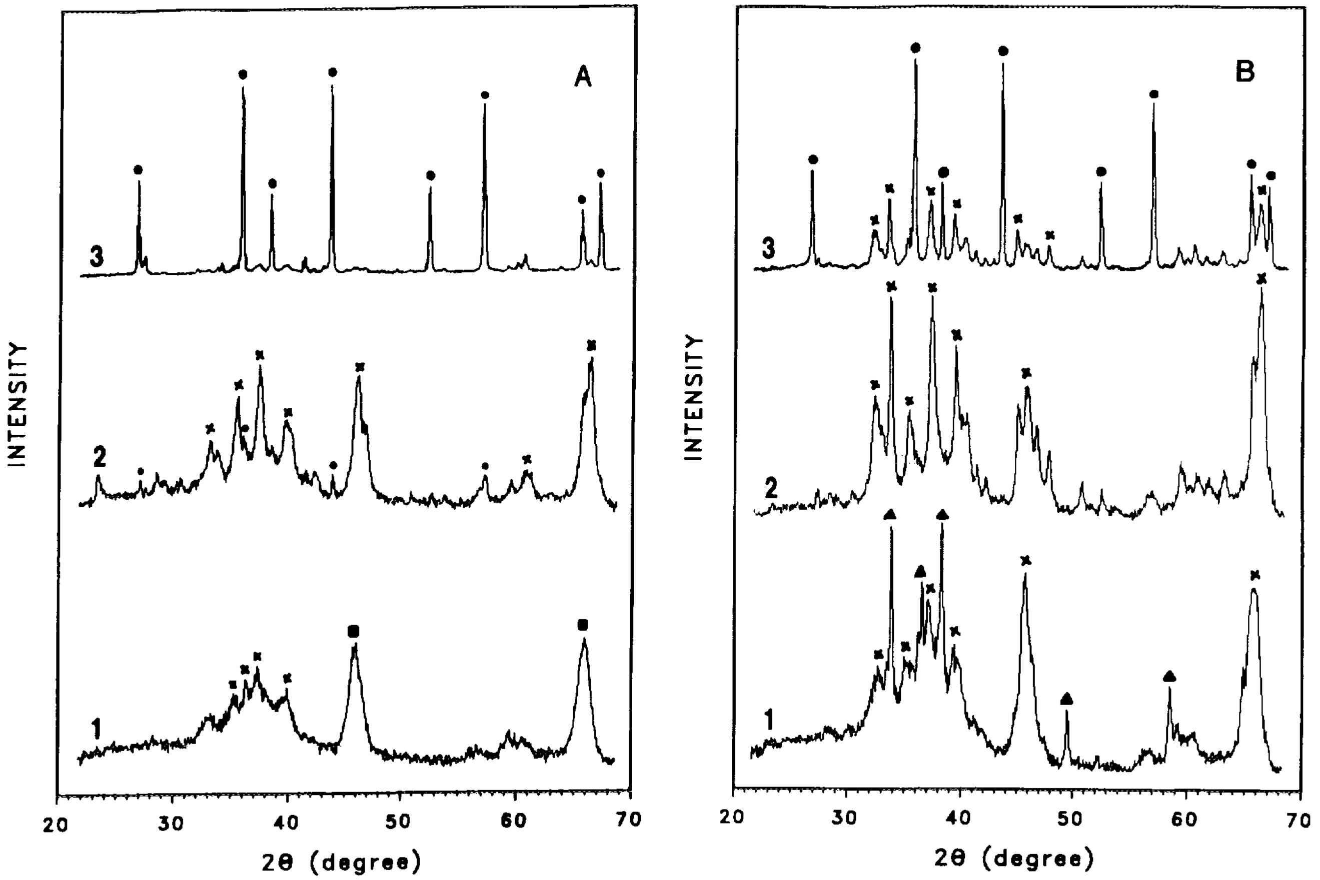

FIG. 1. XRD diagrams of alumina prepared by heating spheroidal (A) and fibrous (B) precursor in a carbon matrix at 2000 K and subsequent calcination in air at 1073 (1), 1473 (2), and 1623 (3) K: (▲) AlN, (●) α-Al_2O_3, (×) δ-Al_2O_3, and (■) γ-Al_2O_3.

TABLE 2

Crystalline Phases of Al_2O_3 Observed During Calcination of the Samples

Calcination temperature (K)	Spheroidal precursor		Fibrous precursor	
	In carbon matrix	Without carbon matrix	In carbon matrix	Without carbon matrix
1073	γ + trace of δ	γ	δ + trace of AlN	γ + trace of δ
1273	$\gamma + \delta$	$\theta + \delta$	δ	θ + trace of δ
1473	δ + trace of α	α	δ	α
1573	$\delta + \alpha$	α	δ + trace of α	α
1623	α	α	α + trace of δ	α

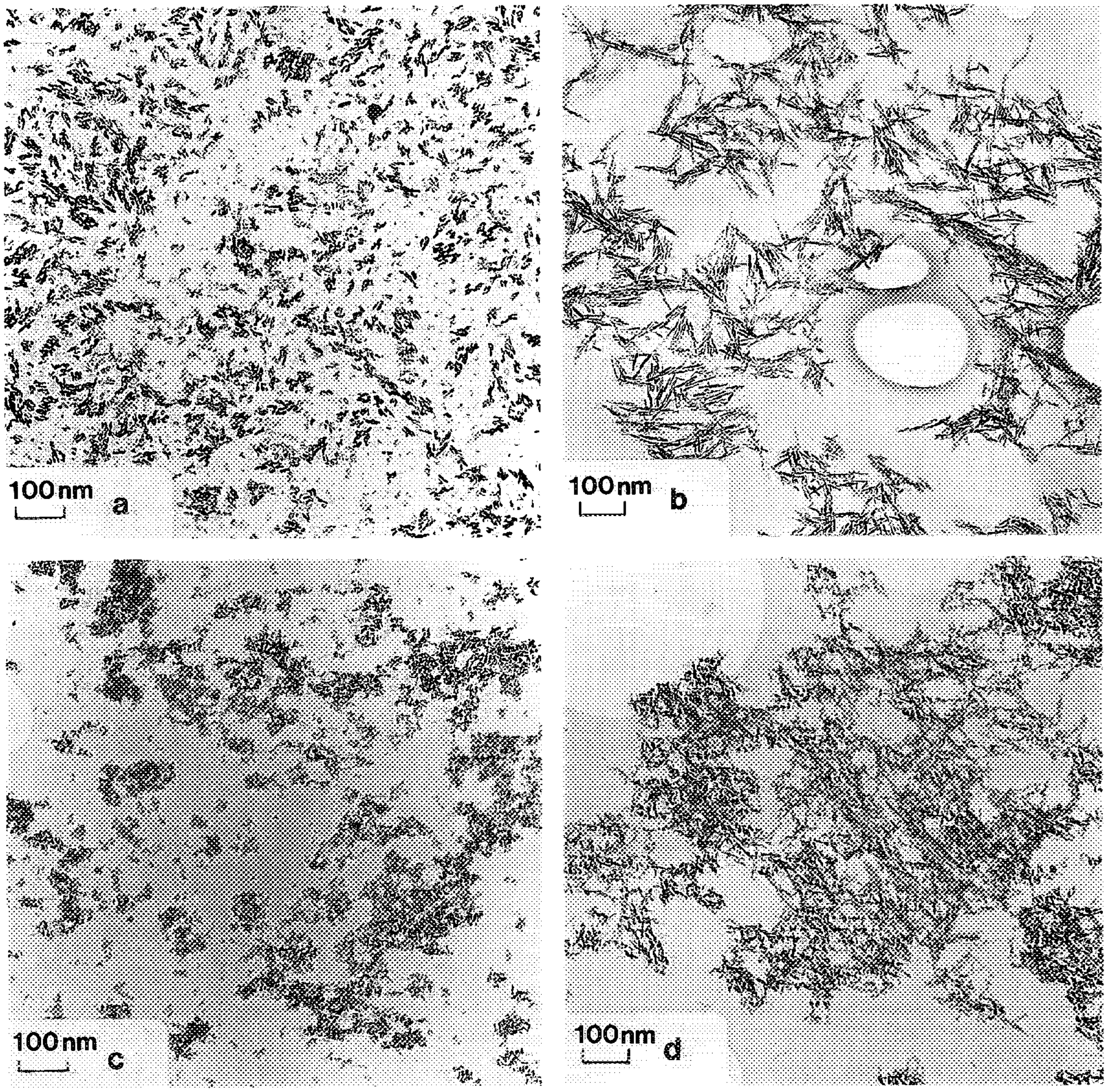

FIG. 2. (a) and (b) The electron micrographs of the dried spheroidal and fibrous precursors; (c)–(h) those of the samples of Al_2O_3 with different precursors, prepared via carbon matrix and subsequently calcined in air at (c)–(d) 1073, (e)–(f) 1473, and (g)–(h) 1623 K.

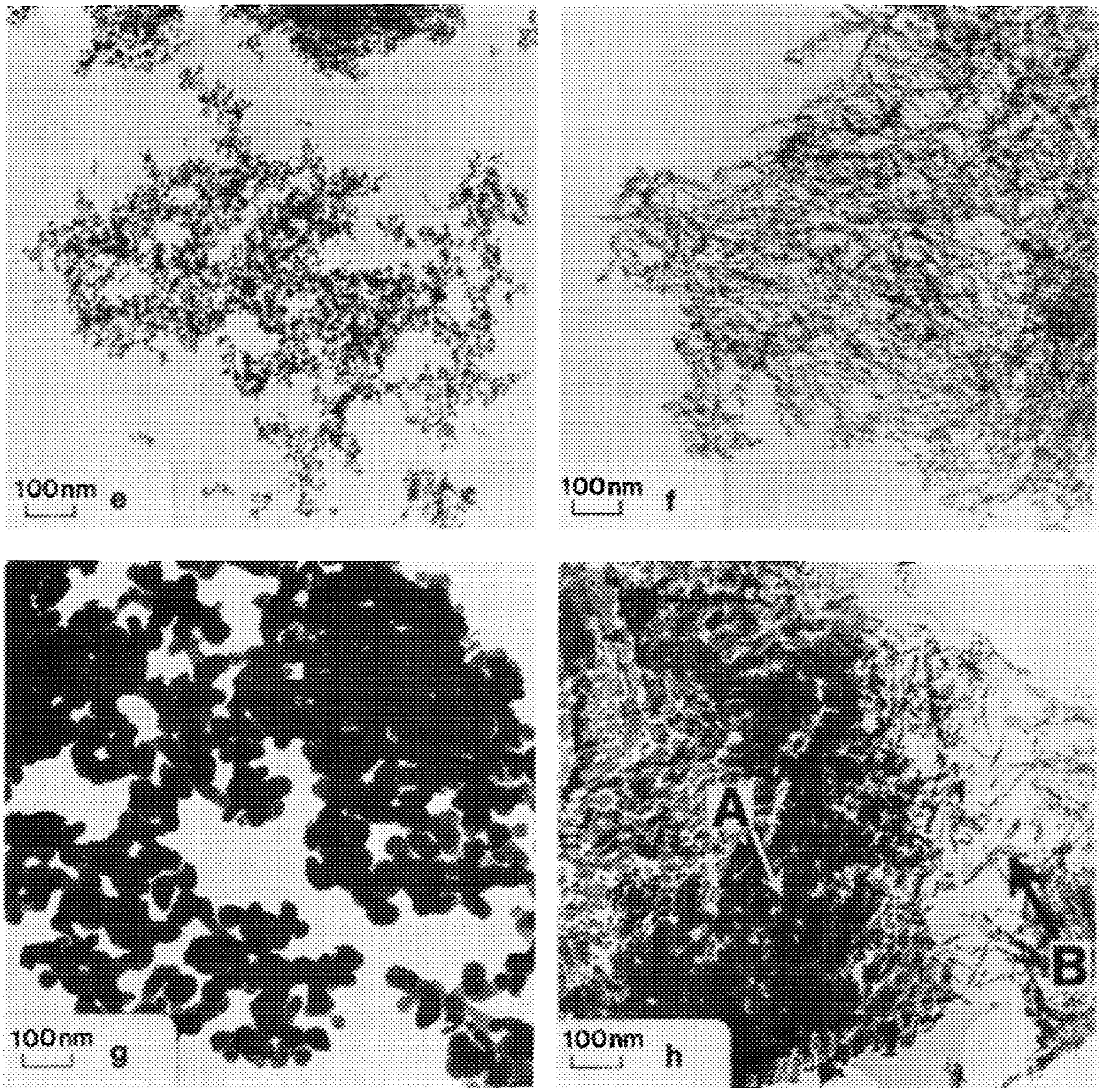

FIG. 2—*Continued*

In general, the samples which were first heated in a carbon matrix at 2000 K and subsequently calcined in air at 1473 K or higher have much larger specific surface areas compared to the samples calcined directly in air at the same temperatures. The drastic decrease of the specific surface area at 1473 K for the samples prepared without the carbon matrix is attributed to the formation of the corundum phase.

The samples prepared by heat-treatment in a carbon matrix appear to be more stabilized than those calcined directly. The samples prepared from the fibrous precursor seem to be more stabilized compared to their spheroidal analogues.

Figure 1 shows the diffractograms of the samples heated in a carbon matrix to 2000 K, subsequently burned at 1073 K, and then calcined at 1073, 1473, and 1623 K, respectively. Table 2 gives the crystalline phases observed after calcination, both for samples prepared with and without the carbon matrix.

The sequences of phase transitions in the samples prepared without the carbon matrix are similar: for both precursors corundum was obtained after calcination at 1473 K. The crystallite diameters (derived from line broadening of the diffraction peak at $2\Theta = 25.60°$) were 70 nm and 62 nm, respectively, for the sample with spheroidal and fibrous precursors, respectively. The formation

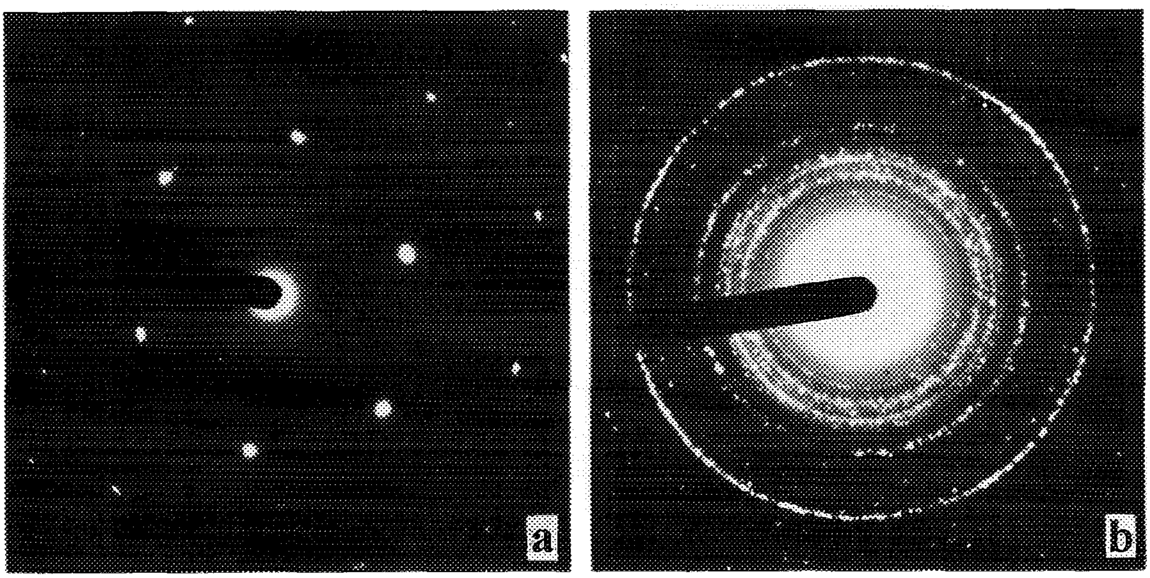

FIG. 3. Electron diffraction patterns obtained from regions marked as zones A and B in Fig. 2h using a selected-area diffraction aperture of 0.25 μm: (a) for zone A and (b) for zone B.

of the α phase at this temperature is responsible for the rapid decrease in specific surface area, as shown in Table 1.

Increasing the temperature to 1623 K results in growth of crystallites of corundum up to 98 nm and 88 nm for the samples with spheroidal and fibrous precursors respectively.

XRD diagrams of the specimens obtained via the carbon matrix is shown in Figs. 1a and b. After burning the carbon matrix at 1073 K, the sample with the spheroidal precursor was mainly composed of the γ-Al_2O_3 phase. On the other hand, in the sample with the fibrous precursor δ-Al_2O_3 and a small amount of AlN phases were detected. Hence, the surface area of this sample should be smaller in comparison with a sample with spheroidal precursor (Table 1). Stabilization of the δ-Al_2O_3 phase can be seen, in particular for the sample with the fibrous precursor, for which no peaks corresponding to α-Al_2O_3 were observed in the XRD diagram after calcination at 1473 K for 3 h. This means that the phase transition to α-Al_2O_3 is hindered. The transition temperature reported in the literature is 1373 K (15).

In the case of Al_2O_3 with the spheroidal precursor there was a trace of α-Al_2O_3 observed in the X-ray diffraction pattern after calcination at 1473 K. A well-defined α phase appears at 1623 K, with a crystalline diameter of about 75 nm, while in the case of the sample with the fibrous precursor the size is 66 nm at the same calcination temperature.

Electron microscopy pictures of Al_2O_3 samples with different precursors prepared via the carbon matrix, and subsequently calcined in air at 1073, 1473, and 1623 K are shown in Figs. 2c–2h, respectively. The TEM pictures of the two precursors are shown in Figs. 2a and 2b.

In general, the morphology of both samples was not changed much after heating at 2000 K and burning the carbon matrix at 1073 K. Obviously, sintering did not occur within the carbon matrix because there was no contact between the alumina particles.

After calcination at 1473 K, both quasi-spheroidal and fibrous particles were observed in the sample prepared in the carbon matrix. Increasing the calcination temperature leads to larger crystallites, but their shape is still conserved. Although no effect of sintering can be observed even after calcination at 1573 K, at higher temperatures (1632 K) the effects of sintering and the presence of dense Al_2O_3 are detected. XRD-analysis of the samples calcined at 1623 K show that the dominating phase was α-Al_2O_3, although in case of the sample with the fibrous precursor the δ phase was also detected. This was confirmed using electron diffraction shown in Figs 3a and b, which were obtained from the zones A and B, as marked in Fig. 2h.

The diffraction pattern of region A in Fig. 3a is a sharp single-crystal pattern and was shown to be α-alumina; there is only very little arcing or splitting of diffraction spots. Electron diffraction patterns of regions similar to B in Fig. 2h became increasingly spotty on decreasing the diameter of the selected area diffraction aperture. This suggests that these regions consist of fine discrete grains. The d-spacings worked out from these rings corresponded well with those of the δ phase of alumina.

TEM and XRD investigations of Al_2O_3 samples prepared via the carbon matrix show clearly that during phase transitions the α phase nucleates and grows in excess of the δ phase, similarly to the "normal" samples. However, the nucleation of the corundum phase occurs at much higher temperatures and is "slower" (i.e., occurs in a wider range of temperature). Heating of alumina in a carbon matrix yields high dispersion after calcination at higher temperatures.

The mechanism and role of the carbon matrix is not clear so far. Initially its presence probably slows down the sintering of Al_2O_3 grains because there is less contact between them. Moreover, during heat treatment of Al_2O_3 in a carbon matrix aluminum nitride is formed, and probably carbides, the latter subsequently being transformed to oxycarbides and oxynitrides during firing (11, 16). The presence of traces of aluminum nitrides was detected in diffraction diagram No. 1 in Fig. 1B. Formation of such compounds at 2000 K is possible (8), as well as subsequent formation of high-temperature resistant solid solutions of $AlN–Al_2OC$ (11).

Concluding the heat treatment of Al_2O_3 dispersed in a carbon matrix at 2000 K in an argon atmosphere (with small traces of nitrogen) leads to the formation of products with increased specific surface areas compared to the samples prepared without a carbon matrix. Furthermore, the phase transitions to corundum are hindered, and the products show increased thermal stability during calcination above 1473 K. Accordingly, they are interesting materials as catalyst supports for use in high-temperature processes.

ACKNOWLEDGMENT

The research was performed under financial support from the State Committee for Scientific Research under Grant 300829101.

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