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NOTE

Large Pore Alumina

Preparation conditions are described for a bimodal alumina having uncommonly large macropores plus appreciable surface area in mesopores. This material is of interest for hydrocracking vacuum residuum molecules in heavy oils and bitumens, some of which can have molecular diameters (d_M) in the 2–4-nm range (1). These sizes are based on measured molecular masses in the 1000–5000 range (2) and on molecular shapes that are flat discs (1). The IUPAC definitions (3) of macropores (pore diameter, $d_{MAP} > 50$ nm) and mesopores (50 nm $> d_{MEP} > 2$ nm) are used here. The large macropore diameters permit the rapid diffusion of the liquid phase vacuum residuum molecules, while the surface area of the mesopores provides the reaction sites. Baltus and Anderson (4) have reported experimental results showing the range of pore sizes in which diffusion of residuum molecules are hindered. An equation describing the liquid phase effective diffusivity of these molecules in terms of the ratio d_M/d_P has been developed and shown to fit the experimental data (5). Recently, Lee *et al.* (6) measured hindered diffusion in catalysts at high-pressure catalytic hydroprocessing conditions. For unimodal catalysts increasing the catalyst pore diameter to increase the diffusion rate will decrease the catalyst surface area that contains the reaction sites. This causes the optimum conversion of residuum molecules to be obtained with catalyst pore diameters in which the diffusion rate influences the overall conversion (7). Experiments with bimodal catalysts have shown that, although macropores which are sufficiently large can decrease the length of the diffusion path in the mesopores, both the rate of diffusion in the mesopores and the rate of the surface reaction simultaneously influence the overall conversion (8).

Earlier (9, 10) we reported preparation conditions for an alumina material which contained large diameter macropores (0.1–100 μm). The preparation variable that caused the formation of the uncommonly large macropores was the large acid/alumina ratios which were very much greater than the ones used in the preparation of conventional porous aluminas (11, 12). The alumina material had large BET surface areas (200 m^2/g) and small mercury porosimetry surface areas (1 m^2/g). This indicated that micropores ($d_{MIP} < 2$ nm) were present in the alumina, since they were large enough for nitrogen gas molecules to enter, but too small for mercury to enter. As a result they would be too small for significant diffusion rates of residuum molecules. In earlier work, the calcining temperature was fixed at 500°C. In the current work, variations in both calcining temperature and calcining time were used in an attempt to convert some of the micropores into mesopores.

Each batch of material was prepared by mixing 100 g of α-alumina monohydrate (SB-alumina powder obtained from Conoco) having a total water content of 25%, with 900 mL (1280 g) of 70% nitric acid. SB-alumina is a very pure material which according to the manufacturer's specifications is a boehmite crystalline phase having impurity levels less than 0.3% carbon, 0.008% SiO_2, 0.005% Fe_2O_3, 0.004 Na_2O, and 0.01% S, and having a particle size distribution of 48% < 45 μm and 11% > 90 μm. The α-alumina monohydrate/nitric acid mixture was allowed to stand for 24 h at room temperature before the excess liquid was decanted from the gel. Then the gels were dried and calcined at the conditions shown in Table 1. It was observed that during the initial drying period, the particles of powder congealed into a hard solid having the shape of the container. This could be avoided by occasionally breaking the solid into smaller pieces during the initial stages of drying. In the earlier work (9) the material that had been dried but not calcined produced an X-ray diffraction spectrum containing many peaks, some of which were similar to the X-ray pattern for aluminum nitrate. The X-ray pattern of the material calcined at 500°C (9) contained a broad peak indicative of an amorphous material, but its peak intensity was only 10% of the peak intensity from γ-alumina (9), suggesting that most of this alumina had a structure that may be different from γ-alumina.

Table 1 shows the pore dimensions of several of these alumina materials that were dried and calcined at conditions that covered a greater range than those reported in the previous work (9). A particle size effect is shown in the first two columns. When the particle size was decreased, the total pore volume increased and the mesopores disappeared. This suggested that there may have been some water remaining in the larger particles of the solid after low-temperature drying. The larger particles were then dried for an additional period at a higher tem-

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TABLE 1

Alumina Pore Dimensions Measured by Mercury Porosimetry

Sample number	1	2	3	4	5	6
Particle Size—mm	+2	−0.074	+2	+2	+2	+2
—mesh no.	+10	−200	+10	+10	+10	+10
Calcining temperature (°C)	450	450	450	800	800	1000
Calcining time (h)	4	4	4	2.5	10.5	8
Drying (1) time temp (°C/h)	70/168	70/168	70/168	70/168	70/168	70/168
(2) time temp (°C/h)	90/384	90/384	90/384	90/384	90/384	90/384
(3) time temp (°C/h)			105/24	105/24	105/24	105/24
Total pore volume (mL/g)	0.48	0.694	0.659	0.742	0.804	0.814
Median mesopore dia (nm)	15	none	none	5.7	3.6	18

perature, 105°C. Column 3 shows that this material had no mesopores and that its total pore volume was similar to that of the small particles in Column 2. This indicated that grinding the material to a very fine powder could be avoided by including a further higher temperature drying period to remove most of the remaining water.

The upper part of Fig. 1 shows the macropore diameters, d_{MAP}, of the calcined aluminas. Values for maximum (90 μm), median (7 μm), and minimum (0.3 μm) macropore diameters did not vary substantially as the calcining temperature increased. However, the lower part of Fig. 1 shows that the volume of macropores, V_{MAP}, in the aluminas did increase substantially as the calcining temperature increased. It also suggests that the calcining time had little effect on macropore volume.

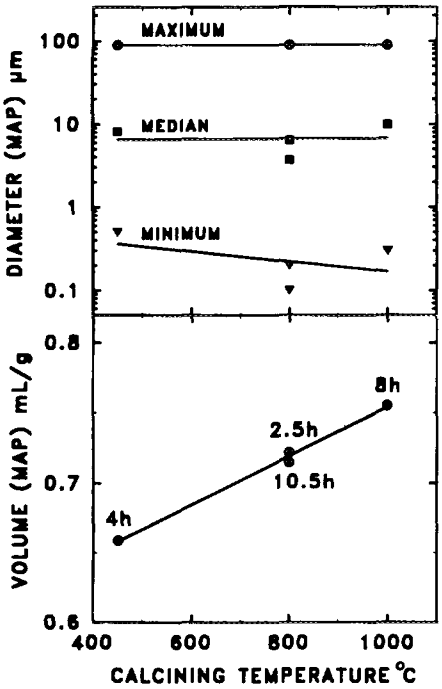

FIG. 1. Upper part: diameter of macropores (μm) versus calcining temperature (°C). Circles, squares, and triangles represent maximum, median, and minimum macropore diameters respectively. Lower part: volume of macropores (mL/g) versus calcining temperature (°C). The numbers shown beside each of the points are the calcining times.

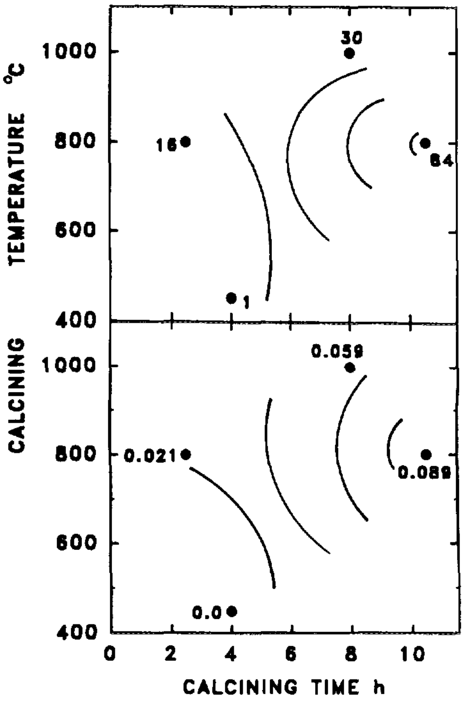

FIG. 2. Calcining temperature (°C) versus calcining time (h). Upper part: Contour lines of constant total surface area measured by mercury porosimetry have been drawn at 20, 40, 60, and 80 m²/g. The numbers shown beside each of the points are the measured surface areas. Lower part: Contour lines of constant mesopore volume (mL/g) have been drawn at 0.02, 0.04, 0.06, and 0.08 mL/g. The numbers shown beside each of the points are the measured mesopore volumes.

Contour lines of constant total surface area, measured by mercury porosimetry, at approximately 20, 40, 60, and 80 m²/g have been drawn in the upper part of Fig. 2, as a function of calcining temperature and calcining time. The lower part shows contour lines of constant mesopore volume at 0.02, 0.04, 0.06, and 0.08 mL/g. The shapes of the two sets of contour lines are similar, since almost all of the surface area accessible to mercury is located in mesopores, rather than macropores. The contour lines suggest that the optimum calcining temperature may be in the neighborhood of 800°C, and that increasing the calcining time increases the mesopore volume.

The combination of large macropore volumes, shown in Fig. 1, and acceptable surface areas in mesopores, shown in Fig. 2, indicate that this alumina should be useful for reactions with large molecules such as those in vacuum residuum. This alumina is definitely different than conventional γ-alumina. Conventional γ-alumina does not contain the large macropores that are in this material. Furthermore, calcining temperatures of 800–1000°C cause the mesopore surface area in γ-alumina to decrease. In contrast the mesopore surface area of this alumina increased after calcining at these temperatures.

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Marten Ternan

Energy Research Laboratories/CANMET
Department of Natural Resources Canada
Ottawa, Ontario, K1A OG1, Canada

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