Electron Microscopy of Porous Materials

The Structure of a Commercial Alumina Catalyst Support*

Supported catalysts have been used for decades both industrially and for fundamental laboratory investigations (*1*). They are useful because of their good thermal stability and high metal surface areas. However their activity depends not only on the chemical properties of the metal and support, but also on the physical properties of the support such as surface area, pore volume, and pore shape (*2*). Indirect information on the pore structure of the support can be obtained from gas adsorption or desorption and from mercury porosimetry experiments, but electron microscopy is a more direct way of obtaining this information (*3*).

FIG. 1. Alumina specimen prepared by ion-milling showing larger voids and fibrous texture; ×101,250.

A number of specimen preparation techniques are available which allow the structure of the support to be examined. These techniques are mentioned briefly below, but more comprehensive descriptions can be found in standard textbooks (*4*, *5*). The

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material can be crushed and dispersed in a solvent, the large particles allowed to settle, and a drop of supernatant liquid allowed to evaporate on a carbon support film. This procedure allows any microstructure to be examined, but the larger voids or macropores are often destroyed.

Surface replication is widely used to examine surface peculiarities. It is a popular method for studying polished, etched, or fractured surfaces. However single-stage replication is unsuitable for catalyst materials, due to the re-entrant nature of the surface and the relative chemical inertness of many supports. The resolution of two-stage replicas is largely governed by the plastic replicating medium used, and is invariably greater than 5 nm. The re-entrant nature of the surface also limits the usefulness of this technique because of difficulties in interpreting the micrographs. In any case, replication is rather an indirect method of examining surfaces.

Several authors (*6*, *7*) have examined surfaces directly by sectioning the material with an ultramicrotome. Although this technique gives a great deal of useful information, it tends to modify the structure of these hard, brittle, and extremely fragile materials. It also produces a great deal of debris, so that care must be taken in interpreting results.

The scanning electron microscope has been used successfully in studies of catalyst systems (*3*). Specimen preparation is easy, although nonconducting materials must be coated with a thin film of metal. The instrument itself is also easier to operate than the transmission electron microscope. However optimum resolution with conven-

FIG. 2. Alumina specimen prepared by ion-milling showing the fine microstructure in a denser region; ×116,250.

tional instruments is about 20 nm, which is insufficient for examining much of the structure.

In an attempt to prepare samples in which the entire micro- and macrostructure would be observable on the same specimen, we have used the technique of ion bombardment thinning, or ion-milling, to prepare samples of catalyst support. This technique has been successfully used in ceramic studies (*8*). The material chosen for this initial study was a high porosity alumina pellet manufactured by Engelhard. The pellet was a $\frac{1}{8}$ in. right cylinder. The pore distribution data as supplied by the manufacturer gave 0.24 cm^3 of pores/g in the range 0–10 nm, and 0.16 $cm^3/g > 10$ nm. A thin disc (3 mm diam) was cut from the center of the pellet, perpendicular to the cylindrical axis. This disc was mounted in the rotating holder of a modified Commonwealth Scientific Corp. ion micro-milling machine. The disc was held at a shallow angle (15–20°) to the two opposing energetic (5–8 kV) beams of argon ions operating at a beam current of 40–50 μA each. The ions displaced, or sputtered, atoms from the surface, removing about 1 μ/hr. When a hole was detected in the alumina disc, the disc was removed and examined in an Hitachi HU-200E electron microscope, operating at an accelerating potential of 200 kV. A large area around the hole was sufficiently transparent to allow the structure to be observed.

Typical photographs are shown in Figs. 1 and 2. Large voids are seen between the fibrous particles of alumina. These voids are particularly noticeable at the bottom of Fig. 1. They connect with cracks running parallel to the fibrous structure of the particles and the cracks appear to connect

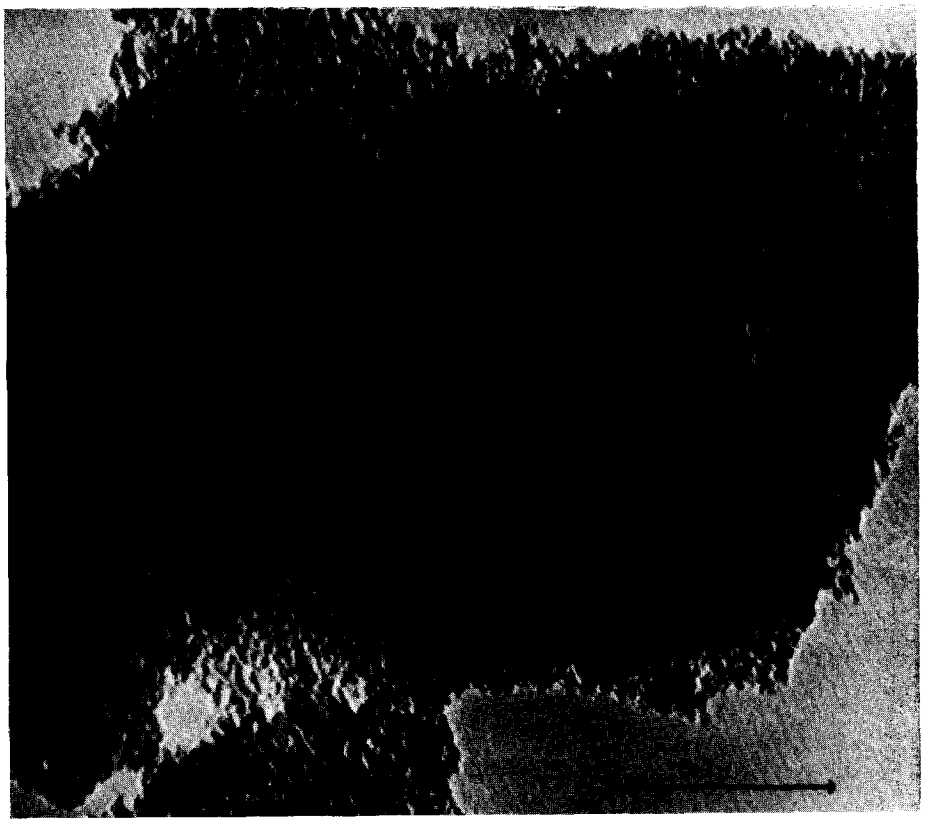

FIG. 3. Alumina prepared by crushing and dispersing on carbon support; ×150,000.

with the fine pore structure of the particles. This fine pore structure, or microstructure, consists of pores of radius about 4 nm and is uniformly distributed throughout the particles.

Figure 3 shows a photograph of a sample prepared by crushing and dispersing the particles on a carbon substrate. The fine pore structure is the only feature observable. This photograph was taken in order to examine the effect of ion bombardment on the fine pore structure, as it was conceivable that the pores could be enlarged significantly during the sputtering process. Since the fine pore structure remains unaltered in specimens prepared by crushing and by ion-milling, it appears that bombardment by argon ions does not change this fine structure. It is still conceivable that ion thinning selectively enlarges the large pore structure. This is very difficult to evaluate. However, in our laboratory ion thinning has been shown to develop no structure at all on single crystals of dense alumina. Barber (*8*) has also noted that irradiation damage caused by ion bombardment is insignificant at lower energies and small angles of incidence similar to those employed here.

Figures 4 and 5 show scanning electron micrographs of portions of a pellet. These were taken on a Cambridge Stereoscan instrument. On the lower magnification micrograph (Fig. 4) the fibrous structure apparent in Figs. 1 and 2 is shown, although no detail can be resolved. A good overall impression of the topography is obtained. At higher magnification (Fig. 5) more detail is resolved. Here the voids and cracks running parallel to the fibrous structure are

FIG. 4. Scanning electron micrograph of alumina pellet (low magnification; ×5850).

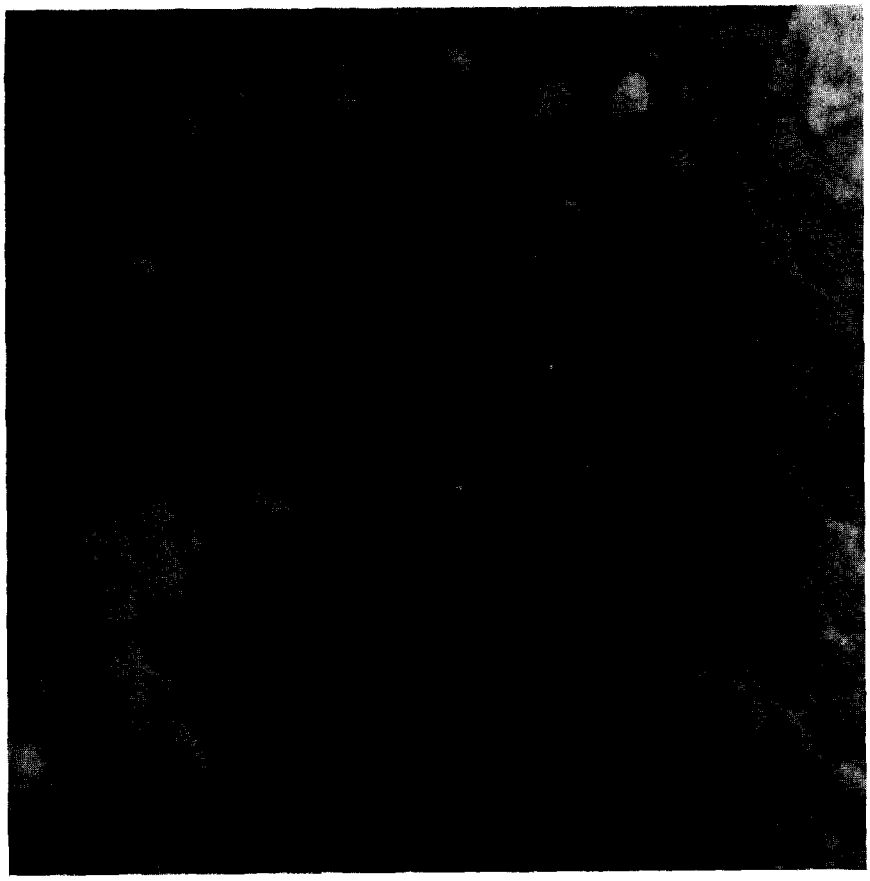

FIG. 5. Scanning electron micrograph of alumina pellet (higher magnification; ×23,400).

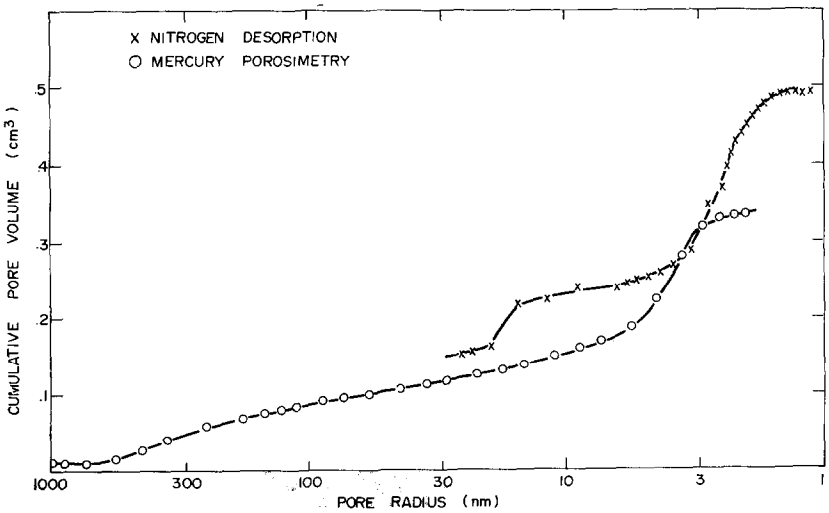

FIG. 6. Cumulative pore volumes of alumina determined by nitrogen desorption and mercury porosimetry.

shown. However the microstructure, and its relation to the macrostructure, are not resolved. As the resolution of our instrument is 20 nm it is clearly impossible to do this. However, as the voids and cracks are visible in the scanning electron micrographs, they are not formed by the ion-milling procedure. Thus the ion-milling technique and scanning electron microscopy complement each other.

Cumulative pore volumes obtained by nitrogen desorption at 77°K and by mercury porosimetry are shown in Fig. 6. The nitrogen data were calculated from isotherms using Dollimore and Heal's method B (*9*). The mercury data were calculated assuming a constant contact angle of 130°. Fine pore radii of 3 to 4 nm are confirmed and there is a pore volume of at least 0.16 cm^3/g of pores with radii greater than 10 nm. This confirms the microscopic observation of many large voids.

The results reported in this note show that ion-milling may be used to advantage to examine the structure of practical alumina pellets. Much of the structure may be examined in a single specimen in the absence of debris and artifacts caused by pressure. The method appears promising for the examination of many catalyst materials, and complements both dispersion work and examination by scanning electron microscopy.

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Volumetric Nitrogen Pore Volume Analysis

INTRODUCTION

Surface area and pore volume are two critical parameters in the characterization of catalysts. Of these parameters surface area is most readily determined by rapid one-point techniques, and one of the most useful of these involves a continuous flow system. Pore volume determinations, however, particularly for the higher pore volumes, are tedious because adsorption at high values of relative pressure (P/P_0) approaches the required equilibrium