

Alumina Substrates with Cylindrical Parallel Pores

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Alumina foils incorporating parallel, cylindrical pores, of about 180 Å diameter, were prepared by anodizing thin (2.5–250 μm) aluminum sheets in oxalic acid at room temperature. Electron micrographs show that pores with narrow size distribution were formed. Such samples may be useful for characterizing mass transport with reaction in catalyst pores in single pellet reactors.

INTRODUCTION

Single pellet reactors offer methods for determining precisely the influence of transport phenomena on reaction rates in porous catalysts (1–4). The pore geometries of the catalysts which have been studied, typical alumina amorphous catalysts, have not been well defined, and it is clear that improved characterization of mass transport influence could be obtained from experiments with catalyst pellets having uniquely defined pore structure.

Anodic oxidation of aluminum surfaces under controlled conditions can produce a film of alumina with a structure of essentially cylindrical, parallel pores (5,6). The pores are closed at one end by a nonporous alumina film, but when the method is used with two sheets of aluminum pressed tightly together, it is possible to produce pores extending across the entire thickness of one sheet. The following paragraphs describe this experimental method and a characterization of the pore structure of the resulting aluminas.

EXPERIMENTAL METHODS

Preparation of Alumina Sheets

Anodic oxidation of aluminum was carried out in a 0.16 M oxalic acid solution at room temperature at a voltage between 10 and 50 V. The distance between the electrodes was 5 cm. Power was obtained from a Hewlett Packard dc power supply Model No. 6200B. The aluminum sheets of 99.999% purity and 2.5–250 μm thickness were used as the anode. The cathode was stainless steel.

Normally the thin alumina film formed on a partially anodized plate of aluminum contains approximately cylindrical pores, which, however, fail to penetrate the entire plate, terminating on a nonporous barrier of alumina. To prepare samples useful for determination of catalytic and transport properties, two aluminum sheets have been pressed together in a plastic holder and anodized from only one side. The nonporous barrier was displaced into the second foil, and the first alumina sheet therefore contained cylindrical pores extending across its entire thickness.

Specimen Preparation for Electron Microscopy

Alumina foils of 2.5–30 μm thickness were thinned at about 50°C by chemical

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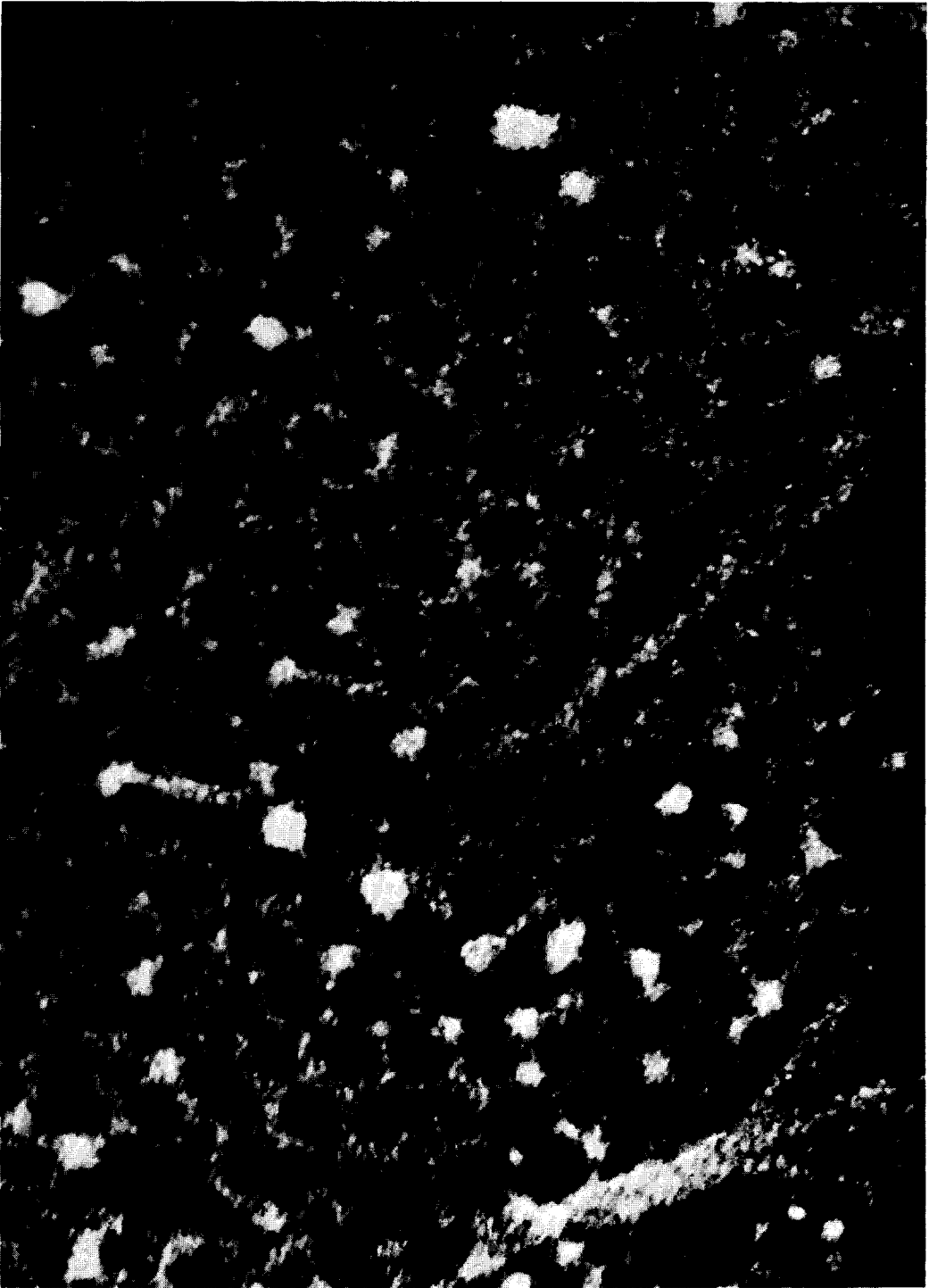


FIG. 1. Scanning electron micrograph of an alumina foil, chemically etched and subsequently coated with Au-Pd alloy film of about 100 Å thickness ($M \times 91,420$) anodizing voltage 45 V.

dissolution into a 40% wt solution of orthophosphoric acid in distilled water. The freshly prepared alumina foils were floated in this solution for 3–10 min, depending upon the initial thickness of the foil. When a sample became sufficiently thin, it was quickly washed in cold distilled water, then dried and mounted on 100 mesh folding nickel grids for electron microscopic examination. The specimens were stored under vacuum to avoid contamination.

Specimens were prepared for scanning electron microscopy by chemically etching them with phosphoric acid solution to remove surface roughness and to increase the pore diameters to a size range which could be resolved by the microscope. After drying in air, the specimens were coated with a film of a Au–Pd alloy of about 100 Å thickness in a vacuum of approximately 5×10^{-5} Torr. This procedure reduces the surface charging effect due to the electron beam and enhances the image contrast.

Metal and Oxide Impregnation

Some of the thin alumina sheets were impregnated with either Ag or MoO_3 . In the former case the freshly prepared dry alumina sheets were immersed in a 1 or 2% wt solution of AgNO_3 in water for 12–24 hr. Subsequently the sheets were air dried and calcined at temperatures near 500°C. In the latter case, 1% wt solution of para-ammonium molybdate in a mixture of 5% wt H_2O_2 in water at a pH between 3.9 and 4.5 was prepared in a manner similar to that described in Ref. (7). Freshly formed alumina sheets, washed with cold distilled water, were immersed in this solution for a few hours at 50–60°C. Following this treatment the sheets were gently washed, air dried at room temperature for 10 hr then at about 120°C for 10 hr, and calcined in air at 500°C for about 12 hr.

RESULTS

Figure 1 shows a scanning electron micrograph of an alumina sample prepared at

an anodizing voltage of 45 V. The corresponding transmission electron micrograph is shown in Fig. 2a. The cross section of each pore is evidently nearly circular. Similar micrographs for other films show that pore-to-pore separation (cell size) increased with the anodizing voltage.

The pore diameters measured from the scanning and transmission electron micrographs (Figs. 1, 2a and 2b) are greater than the diameter of the anodically formed pores, since the thinning of the alumina sheets by chemical dissolution also increases the pore sizes. The pore-to-pore separation was unaffected by the thinning, as expected. The cell size increased linearly with increasing anodizing voltage, as shown in Fig. 3. However, the straight line did not pass through the origin, but had an intercept at about 180 Å which, as suggested in Ref. (8), was interpreted as the pore diameter.

The pore density was inversely proportional to the square root of the anodizing voltage and the anodizing rate increased with increasing voltage. Figure 4 is a plot of pore density and of global anodic oxidation rate vs anodizing voltage. The global anodic oxidation rate was defined as the ratio between the thickness (25 μm) and the time interval for the complete oxidation of a 25 μm thick aluminum sheet at a given anodizing voltage.

At high anodizing voltages (> 15 V) and thick aluminum sheets (> 2.5 μm) the pores form an ordered arrangement of cylinders of approximately equal radii. Figure 5, constructed from measurements taken from several micrographs, shows a statistical distribution of the number of pores lying approximately at first neighbor distance around a pore. The distribution indicates a maximum at six nearest neighbors, indicating the tendency for formation of a hexagonal network. At low voltages (< 15 V) the pores were much closer to each other and distorted. For very thin foils of aluminum (< 2.5 μm), the existing mechanical deformations appeared

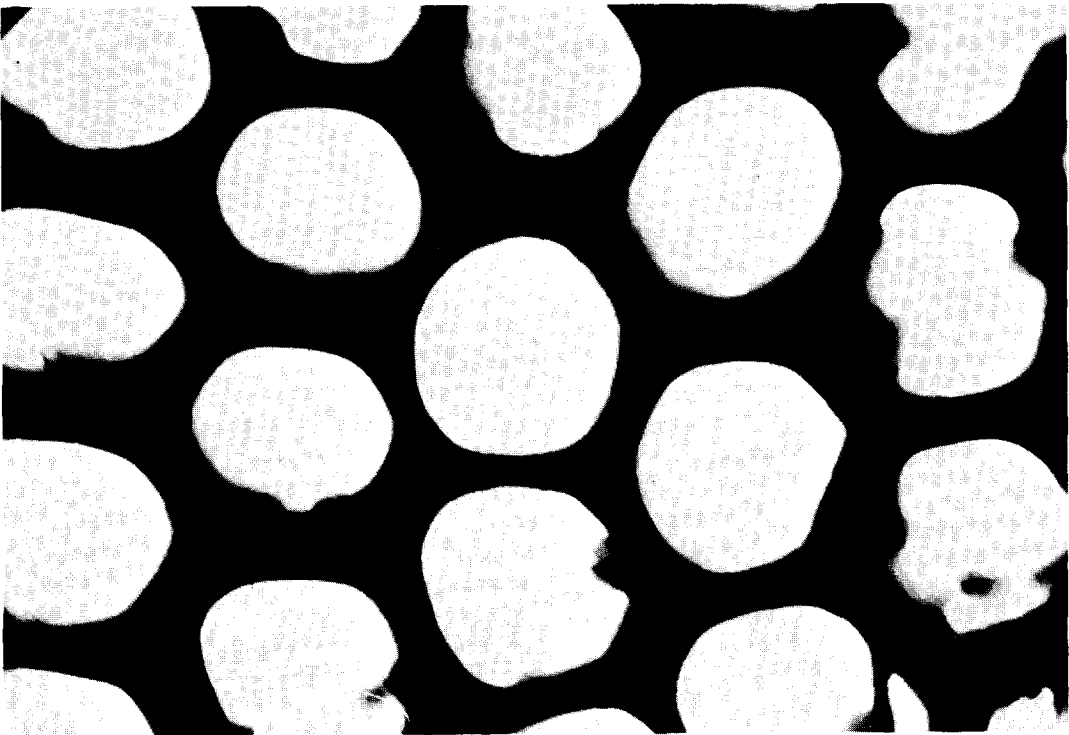
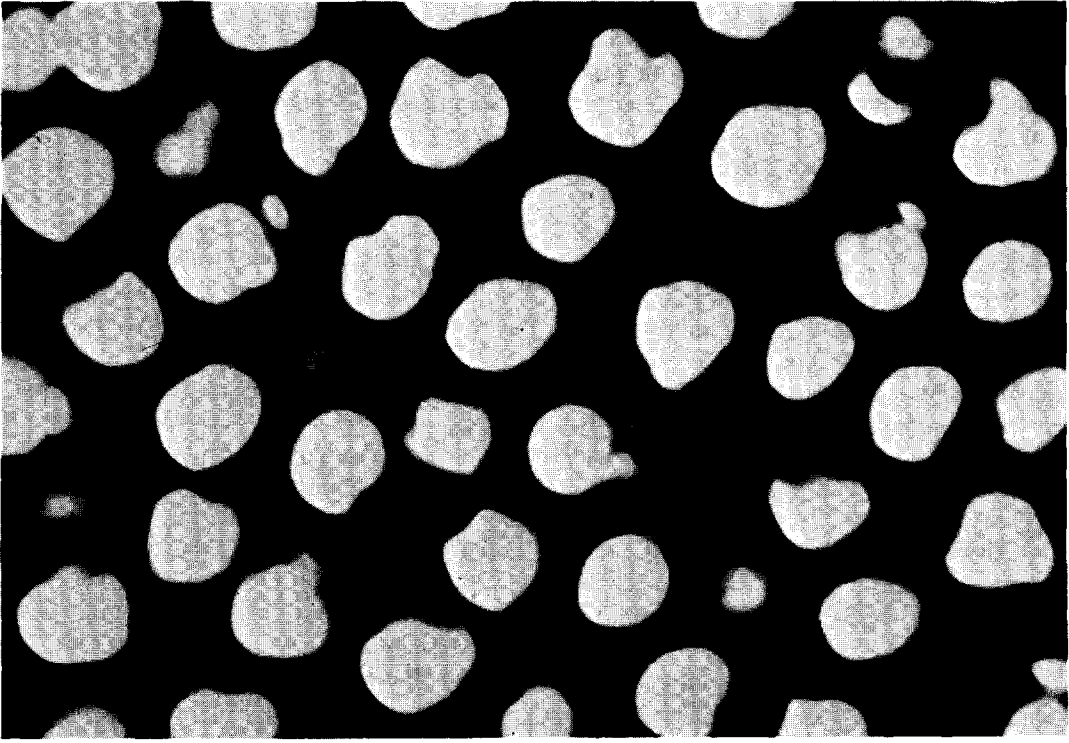


FIG. 2a. Transmission electron micrograph of an alumina foil of 25 μm thinned by H_3PO_4 solution ($M \times 200,000$); anodizing voltage 45 V.
FIG. 2b. Transmission electron micrograph of an alumina foil of 2.5 μm thinned by H_3PO_4 solution ($M \times 200,000$); anodizing voltage 45 V.

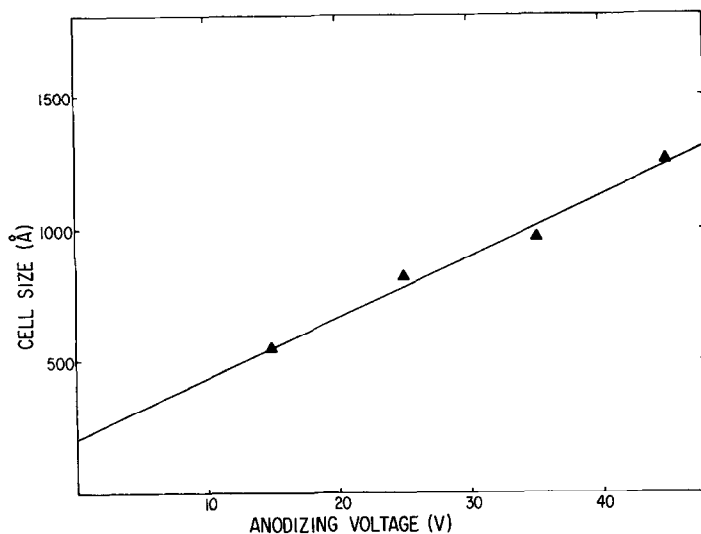


FIG. 3. Dependence of cell size on anodizing voltage for anodization in 0.16 M oxalic acid.

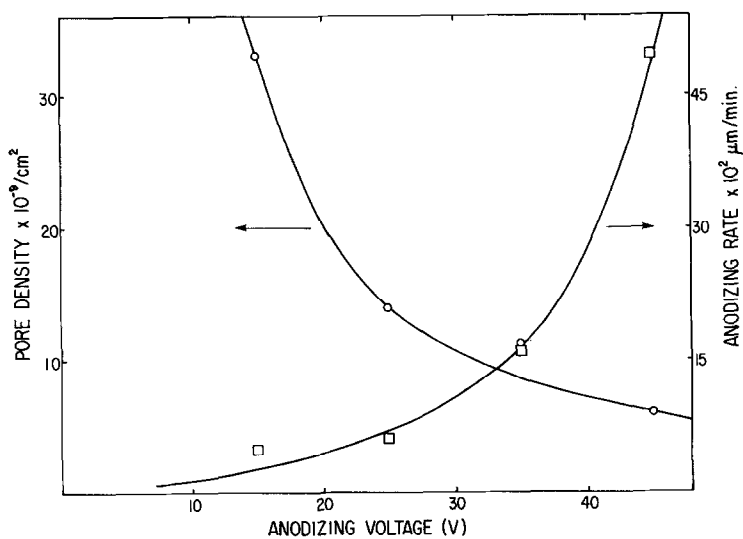


FIG. 4. Dependence of pore density and global anodic oxidation on anodizing voltage.

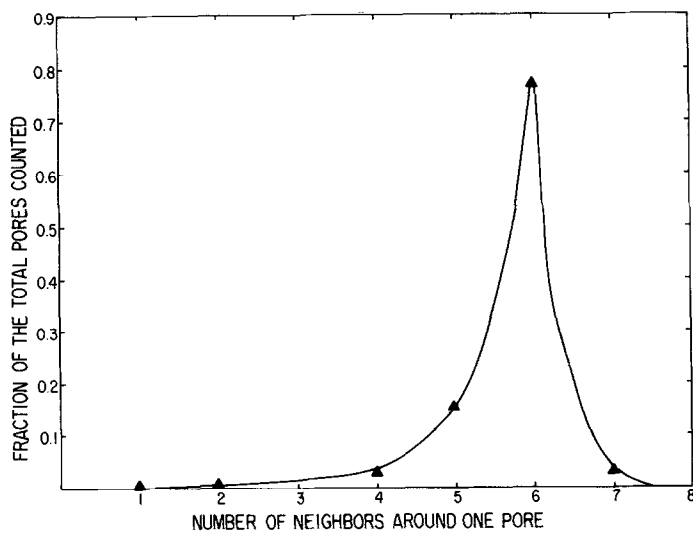


FIG. 5. Statistical distribution of the number of first neighboring pores around a pore.

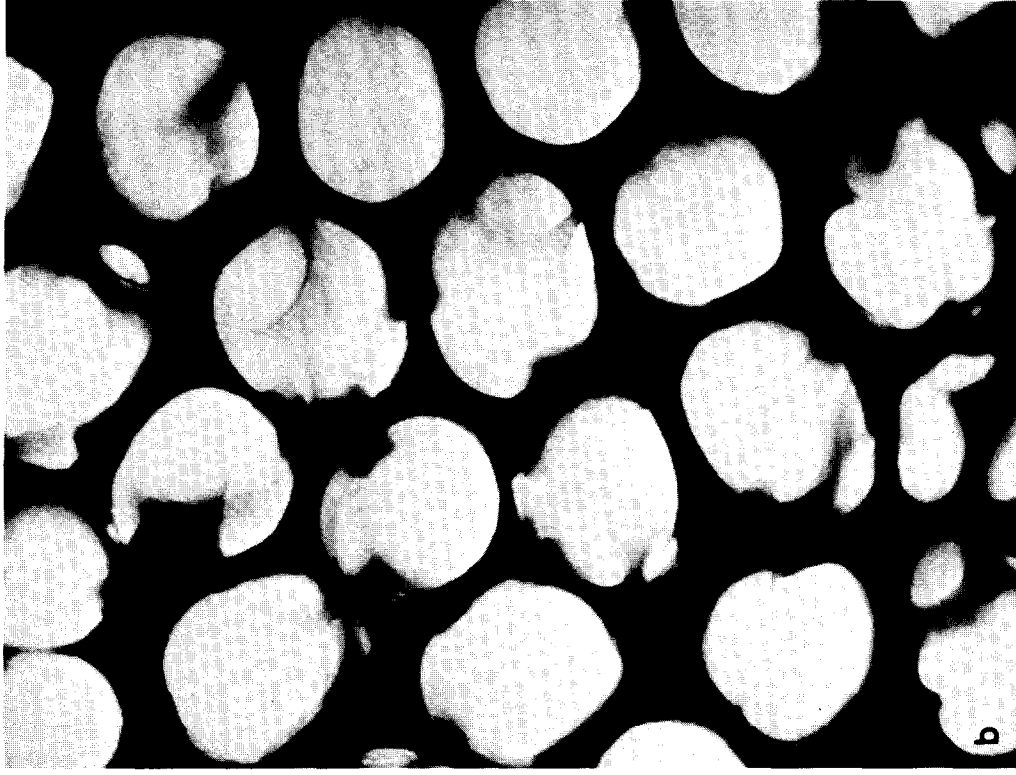
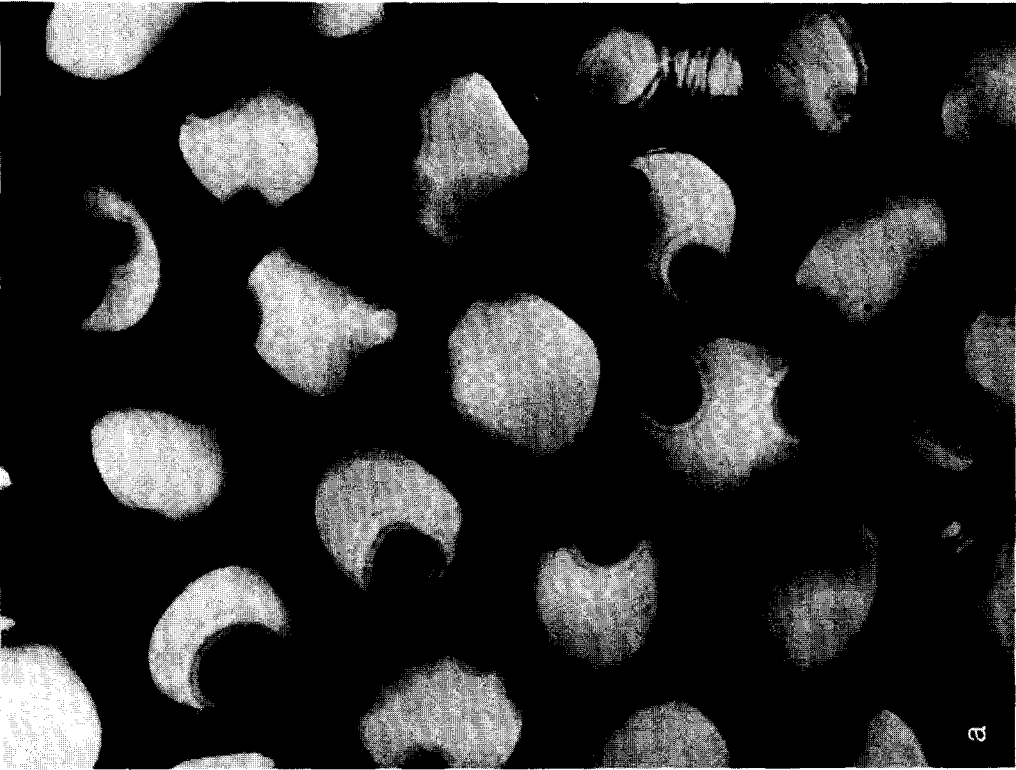


FIG. 6a. Transmission electron micrograph of Ag impregnated alumina ($M \times 210,000$).
FIG. 6b. Transmission electron micrograph of MoO_3 impregnated alumina ($M \times 210,000$).

to affect the distribution of pores, and the distribution was more disordered (Fig. 2b).

The porous alumina prepared in the present investigation had amorphous structure and remained unchanged when held at temperatures greater than 500°C for several days, as demonstrated by the lack of sharp diffraction rings in the electron diffraction pattern. Often few small islands of aluminum of less than about 100 Å are encountered in the electron microscopy studies, especially when the aluminum sheets contained many mechanical deformations, such as visible slipbands.

Transmission electron micrographs of Ag and MoO₃ impregnated thin films of alumina are shown in Figures 6a and 6b.

The alumina sheets prepared by the technique described here may find application for systematic study of heterogeneous catalysis, since they can be tailor-made with clearly defined pore geometries. It has been also observed that if the alumina sheets are sufficiently thin (< 30 μm) they have good transmittance for infrared radiation. Therefore the chemical processes

taking place inside the pore can be studied by infrared spectroscopy.

Note added in proof. In some experiments the aluminum foils have been subjected to γ radiation before anodization to generate active centers for pore formation. No significant effect was observed.

ACKNOWLEDGMENT

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REFERENCES

1. Roiter, V. A., Korneichuk, G. P., Leperson, M. G., Stukanowskaia, N. A., Tolchina, B. I., *Zh. Fiz. Khim.* **24**, 459 (1950).
2. Balder, J. R., Petersen, E. E., *J. Catal.* **11**, 202 (1968).
3. Hahn, J. L., Petersen, E. E., *Can. J. Chem. Eng.* **48**, 147 (1970).
4. Hegedus, L. L., Petersen, E. E., *Ind. Eng. Chem. Fundam.* **11**, 579 (1972).
5. Young, L., "Anodic Oxide Films." Academic Press, London, 1961.
6. Diggle, J. W., Dowme, T. C., and Goulding, C. W., *Chem. Rev.* **69**, 365 (1969).
7. Giordano, N., Bart, J. C., Vagni, A., Castellan, A., and Martinoth, G., *J. Catal.* **36**, 81 (1975).
8. Keller, F., Hunter, M. S., and Robinson, D. L., *J. Electrochem. Soc.* **100**, 411 (1953).