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A New Method for Evaluating the Inner Pore Structure of Porous Catalysts—Resin Replication of Silica

Reaction processes and transport phenomena involving porous catalysts have generally been analyzed by some simple pore structure models; however, it is doubtful whether the models reflect the real pore structure. Nevertheless the pore structures of silica and zeolites have been designed and broadly characterized in relation to their catalytic properties (*1–4*). Surface area measurements with adsorption of various kinds of gases, pore size distribution measurements with mercury, and direct observation of pores by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) have been applied for the characterization. These techniques, however, cannot give any direct information on the shape of the pore structures. Even with SEM, the real pore structure of porous substances having complex internal structure can neither be evaluated nor portrayed from just the micrograph. No model for the pore structure of silica supports has yet been widely accepted (*5*).

In this note, the authors present SEM images of the shapes of a porous silica catalyst support observed by a new resin replication which had been successfully adopted for the visualization of pore structures of porous aluminum electrodes (*6, 7*).

An epoxy resin monomer (Ciba-Geigy Co., Ltd., phenol-novolak epoxy resin "Araldite" XPY-307) was mixed with its hardner (HY-932), and the mixture was evacuated in a vacuum cell at 60°C. A few particles of a porous silica support (Nikki Chemical Co., Ltd., No. E-23H, pore volume: 0.8116 $cm^3\ g^{-1}$) were set in the other half of the vacuum cell and evacuated at 200°C. After these degassing procedures, resin monomer was poured over the silica under vacuum. Then air was admitted into the vacuum cell in order to pack the resin monomer into the inner region of the porous silica support. Next, this resin–silica mixture was heated at 80°C for 10 h followed by heating at 120°C for 4 h to polymerize the resin. This silica–polymer block was cut to expose the silica. Finally the silica was thoroughly dissolved by treatment with an aqueous solution of HF (4%). Only a slight amount of the resin was corroded by this treatment.

Figures 1 and 2 show SEM images of a fracture plane of the silica catalyst support and that of its replica, respectively. One can see that the silica contains various sizes of pores; however, it is difficult to evaluate the pore structure only from the SEM image of Fig. 1. On the other hand, the pore shape could be successfully visualized in Fig. 2. In this replica, no trace of silicon was observed by an X-ray analysis (Phylipps, Co., Ltd., EDAX 9100). In Fig. 3, the pore size distribution of this silica catalyst support determined by a mercury porosimetry is presented. Since the pores of this silica shown in Fig. 2 have no simple cross-sectional shape, direct comparison of the pore size distribution in Fig. 3 with that of Fig. 2 is not easy. A quantitative evaluation method for the "pore shape" is now under investigation, in which the shapes of the cross sections of the pores, the lengths of the boundary of pores and silica, and the ratios of the cross section of pores to that of silica as it appears in this photograph will be statistically treated.

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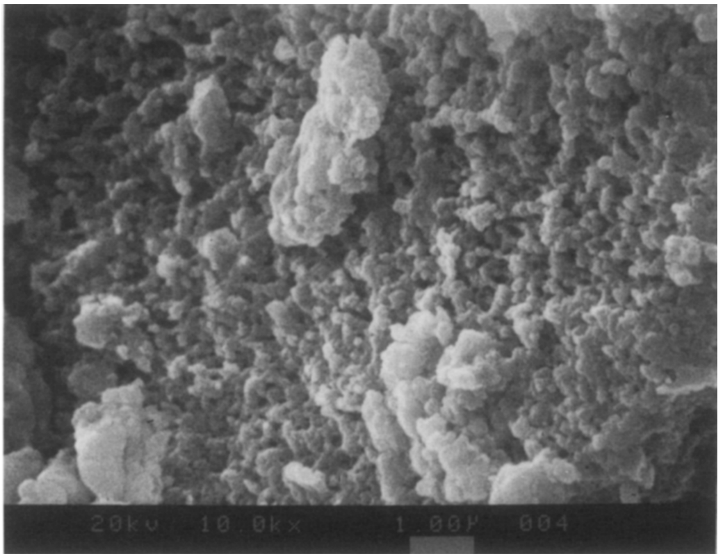

FIG. 1. SEM image of a fracture plane of a porous silica catalyst support (Nikki Chemical Co., Ltd., No. E-23H. Photographed with Akashi ALPHA-30).

The most important point of this new resin replica method is that both the packing material (epoxy resin monomer) and porous samples can be evacuated so that the resin monomer can effectively fill the pores. This makes it possible to reveal the fine structure of porous silica catalyst support. When we used another packing material (Palouse Petro Products Co., Ltd., "Petropoxy 154"), which has often been

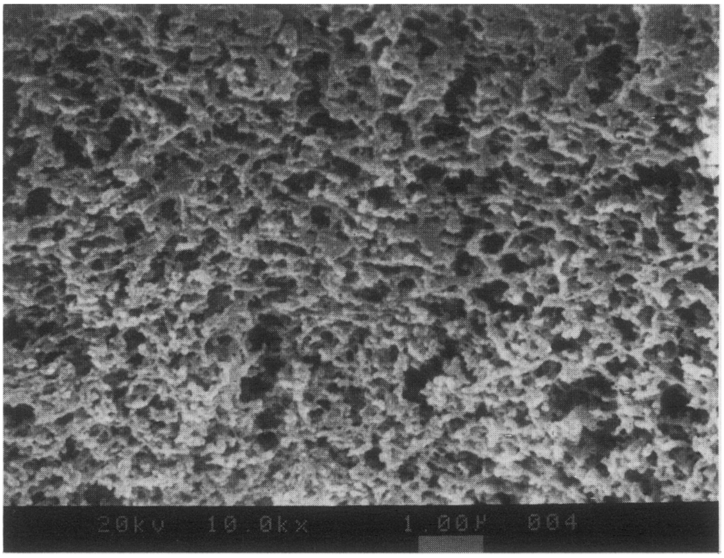

FIG. 2. SEM image of a resin replica of the porous silica catalyst support. (The packing material for this resin replica was Araldite XPY-307. About 20 nm of gold film has been deposited on the replica.)

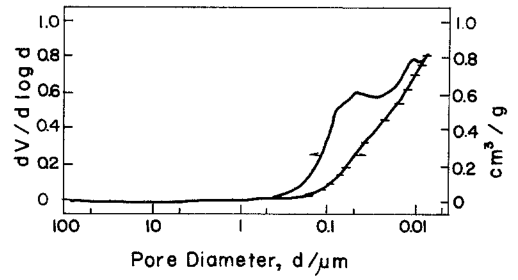

FIG. 3. Pore size distribution of the porous silica catalyst support determined by a mercury porosimetry (measured by Nikki Chemical Co., Ltd.).

employed in the resin replication for minerals (*8*), we could not adequately evacuate it without increasing its viscosity. Moreover, the Araldite resin used here is stable in HCl, H_2SO_4, and water; thus this resin replica method can be used to visualize the pore structures of various kinds of porous materials. The resolution of this method, however, is limited to structures larger than ca. 50 nm, because ca. 20 nm of gold or carbon must be deposited on the replica to avoid electrical charging. The resolution could be improved if a thinner electrically conducting coating material were developed.

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