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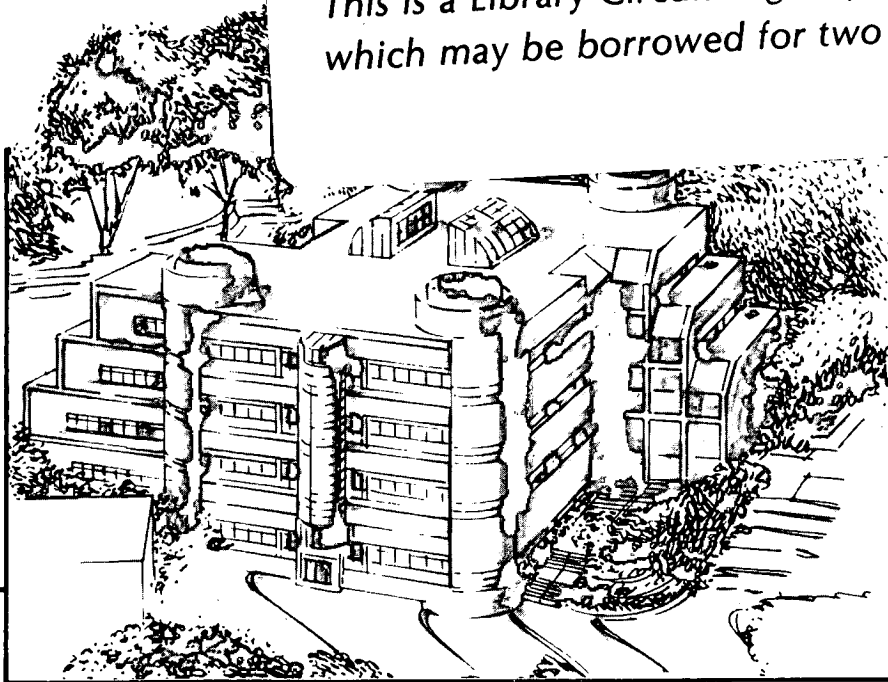
Preparation of Zeolites for TEM Using Microtomy

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PREPARATION OF ZEOLITES FOR TEM USING MICROTOMY

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ABSTRACT

The application of microtomy to Transmission Electron Microscopy (TEM) specimen preparation of zeolite catalysts is explained. Using a new acrylic resin (LR White®) thin sections (≤ 60 nm) may be cut with relative ease. Although the details described are specific to catalysts, microtomy and the use of the acrylic resin are applicable to any hard ceramic powder sample.

INTRODUCTION

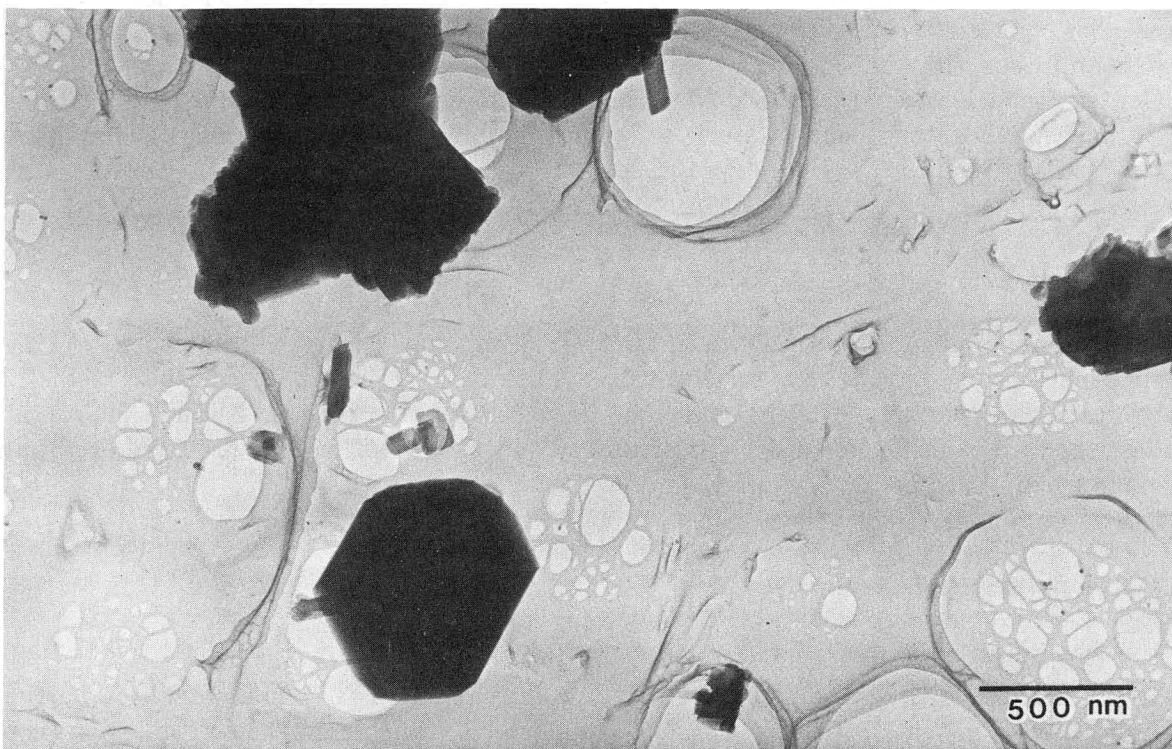
Zeolites are crystalline aluminosilicates possessing regular and uniform pore structures. It is this pore structure and high surface area that make zeolites particularly useful as catalysts and catalyst supports. Transmission electron microscopy (TEM) is particularly useful for studying the structure of these catalysts since traditional surface science techniques are not applicable to internal surfaces.

An easy way to prepare particulate catalyst specimens is to grind and disperse them in an inert liquid and drop this suspension onto a "holey" carbon film supported by a copper grid (see figure 1). Although this is satisfactory for some applications, it seldom produces particles thin enough for good high resolution imaging or spatially resolved analytical electron microscopy. Alternatively, ultramicrotomy [1] may be used to produce good quality, uniformly thin specimens of these powder catalysts. This technique involves embedding the particulates in a plastic resin and slicing electron-transparent sections with a diamond knife.

RESIN SELECTION

The choice of embedding resin is very important to good thin sectioning because the embedded block must present a homogeneous surface to the knife. The resin must penetrate the open spaces in the particles, bind firmly to their surfaces and polymerize to an equivalent hardness. Several authors have used the Araldite 6005 epoxy mixture for aluminum oxide catalyst particles, successfully cutting thin sections (40-100 nm) [2, 3]. Zeolites are more difficult to embed than aluminum oxide. The viscous epoxy resins (e.g., Araldite, Epon, Spurs) neither infiltrate nor bind zeolites well. When sectioning is attempted most particles "tear" out of the block face.

An acrylic resin, LR White® (London Resin Co.) binds well, however, to the zeolites and the particles remain embedded during thin sectioning [4]. The LR White® resin is a particularly attractive embedding medium for several reasons. It is a single component resin, eliminating the need for mixing when heat cured. Its low viscosity, 8 centipoise, allows rapid infiltration of powder samples. An additional plus is that LR White® has a very low degree of toxicity, containing only monomers used in medicine and dentistry, while most epoxy monomers are somewhat mutagenic.



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Figure 1 - Ferrisilicate analog of zeolite ZSM-5 catalyst particles suspended on a "holey" carbon film.

There are two major disadvantages to LR White[®] resin. It will not polymerize well when exposed to oxygen and it penetrates most polyethylene and silicon rubber molds [5]. The effect of oxygen is inconsequential when embedding catalyst particles because the polymerization is complete in one hour at 90° C. However, most biological tissues cannot tolerate the elevated temperature so the curing is done at 60° C for 24 hours in #00 gelatin capsules using a vacuum oven [6]. The penetration of the acrylic resin into the molds is a substantial problem. Polyethylene molds deform during curing and therefore cannot be used. Although penetration into BEEM[®] BOJAX[®] silicon molds occurs using LR White[®], it does not eliminate their use. BEEM[®] BOJAX[®] molds may be used for 3-4 embedments before the infiltration of the resin into the mold renders it useless. Embedding and curing with LR White[®] is best carried out in gelatin capsules to avoid problems with mold infiltration; penetration of LR White[®] into gelatin capsules has not been reported to date.

EMBEDDING AND CURING

The zeolite powder is ground with an agate mortar and pestle to break up any large agglomerates. The powder is then placed in a 1 x 1 mm area in the bottom of BEEM[®] BOJAX[®] molds or gelatin capsules. The molds are one third filled with LR White[®] "hard" grade resin and placed under vacuum (15-20 psi) for 2-4 minutes to

remove air bubbles and enhance good infiltration. The molds are then filled with resin and placed under vacuum again for 1-2 minutes to remove any trapped air bubbles. Although the embedding resin is low viscosity, the polymerization step progresses rapidly and vacuum infiltration is therefore necessary to prevent holes in the cured block.

The filled molds are cured in a 90° C oven for 1 hour. After curing, the part of the block that had been exposed to air during polymerization remains soft, as determined by the "fingernail test"; the rest of the block, not in direct contact with air during curing, is hard and ready for sectioning. When using BEEM® BOJAX® molds, the blocks are removed from the rubber mold by hand and are ready for sectioning. When using gelatin capsules, the block and capsule must be soaked in water for 30 minutes to remove the gelatin capsule before sectioning.

THIN SECTIONING

Before thin sectioning on a microtome, the specimen block must be trimmed so that the final sections are cut from a uniform small area of the block. Catalyst particles are difficult to cut, and a smaller block face results in easier slicing. Trimming may be done by hand using a single-edged razor blade; however, this requires great care and skill since the desired final size of the trapezoid for thin sectioning is generally 0.1 x 0.1 mm. Mechanical trimming of the specimen block may be done using a glass knife on the ultramicrotome as described by Reid [1]. This is recommended because it will give a precisely shaped block face, and the operator need only change from a glass knife to a diamond knife to begin thin sectioning.

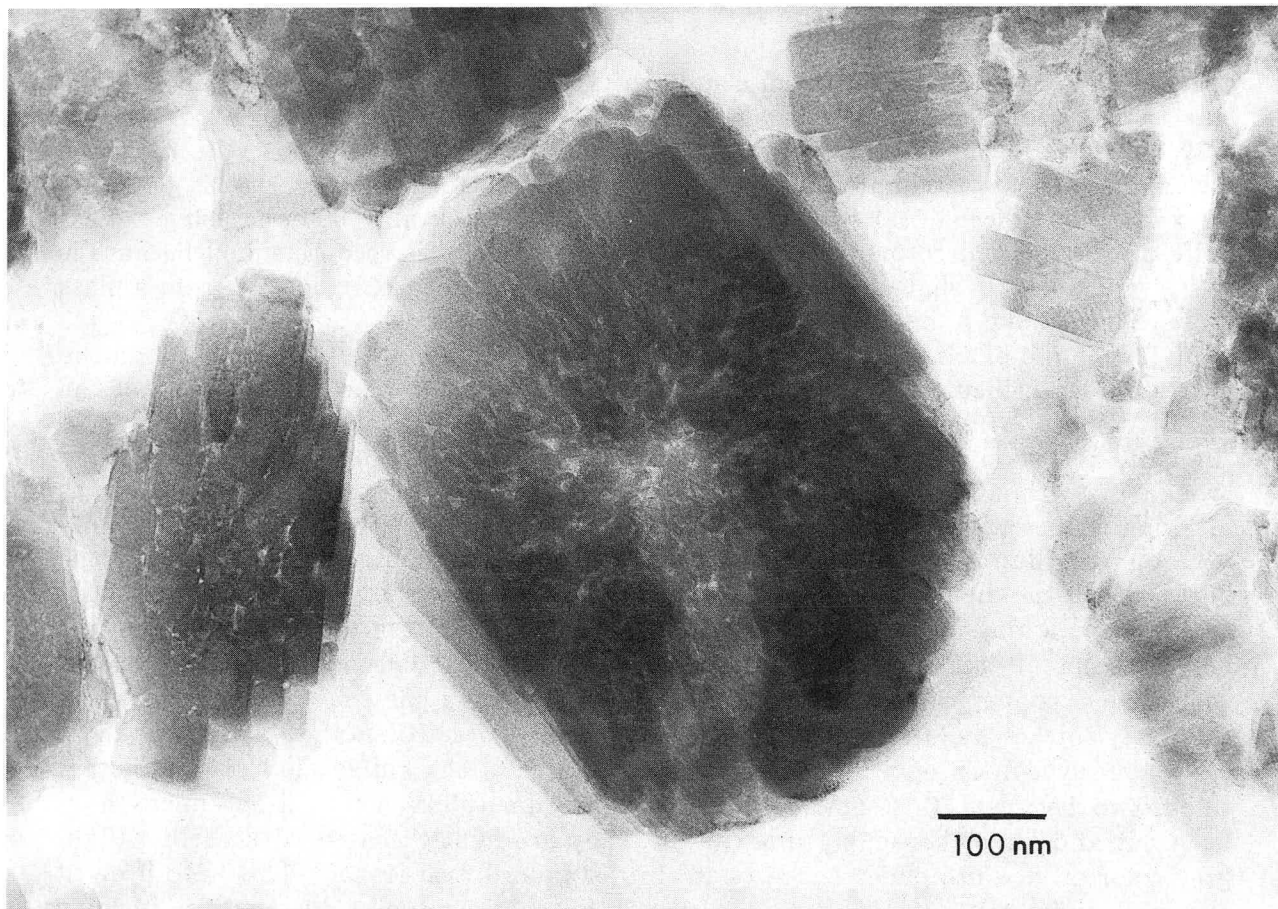
After the block has been faced and trimmed, a diamond knife is mounted on the microtome and filled to the appropriate level with water [1]. The water trough of the diamond knife is filled and adjusted before the knife is moved close to the block to eliminate the possibility of getting water on the block face. The knife is then slowly brought to within 200 nm of the block face. This is facilitated on modern microtomes by using a fiber optically coupled light behind the knife edge; the shadow of the knife edge on the illuminated block face allows accurate alignment of the knife with the block. With the diamond knife position fixed, the automatic block advance is actuated and thin sectioning begins. When the knife is new, the first ten to fifteen sections may be less than 50 nm thick. These are picked up on a 400 mesh rhodium plated "pathfinder" copper grid and allowed to dry. As sectioning continues the slices get progressively thicker due to dulling of the knife edge by the hard catalyst particles. Typically, four specimens may be obtained from one area of the knife; one less than 50 nm thick, two between 50-90 nm thick and one 100 nm thick. After all specimens have been cut and have thoroughly dried in air, they are lightly coated with carbon (light grey color on a white paper background) in a standard evaporator. This is to prevent charging under the electron beam. Although all specimens may be used for imaging and analytical microscopy, the thinnest specimen is best suited for high resolution electron microscopy, while the 100 nm thick sample is better for X-ray emissive spectroscopy.

ADVANTAGES

Particulate catalyst TEM specimens prepared by microtomy have several advantages over those prepared by dispersing powders on a carbon film. Microtomy produces

specimens of uniform thickness, thus structural information is not limited to the edges of a few particles as in dispersed samples (see figure 2). The internal structures of these agglomerates, important to understanding the mechanisms of nucleation and growth of these catalysts, could not be determined using scanning electron microscopy (SEM) or by TEM of dispersed samples, but TEM of a microtomed specimen immediately reveals this structure.

Microtomed samples are usually thin enough (≤ 100 nm) that absorption corrections can be neglected when doing quantitative X-ray emissive spectroscopy (XES) on light element catalysts. In the case of heavier elements where absorption can not be ignored, microtomed samples again are preferred since they closely approximate an ideal slab of uniform thickness. This is in contrast to dispersed specimens where thickness varies and must be determined for each particle, which can range in size from tens of nanometers to several microns.



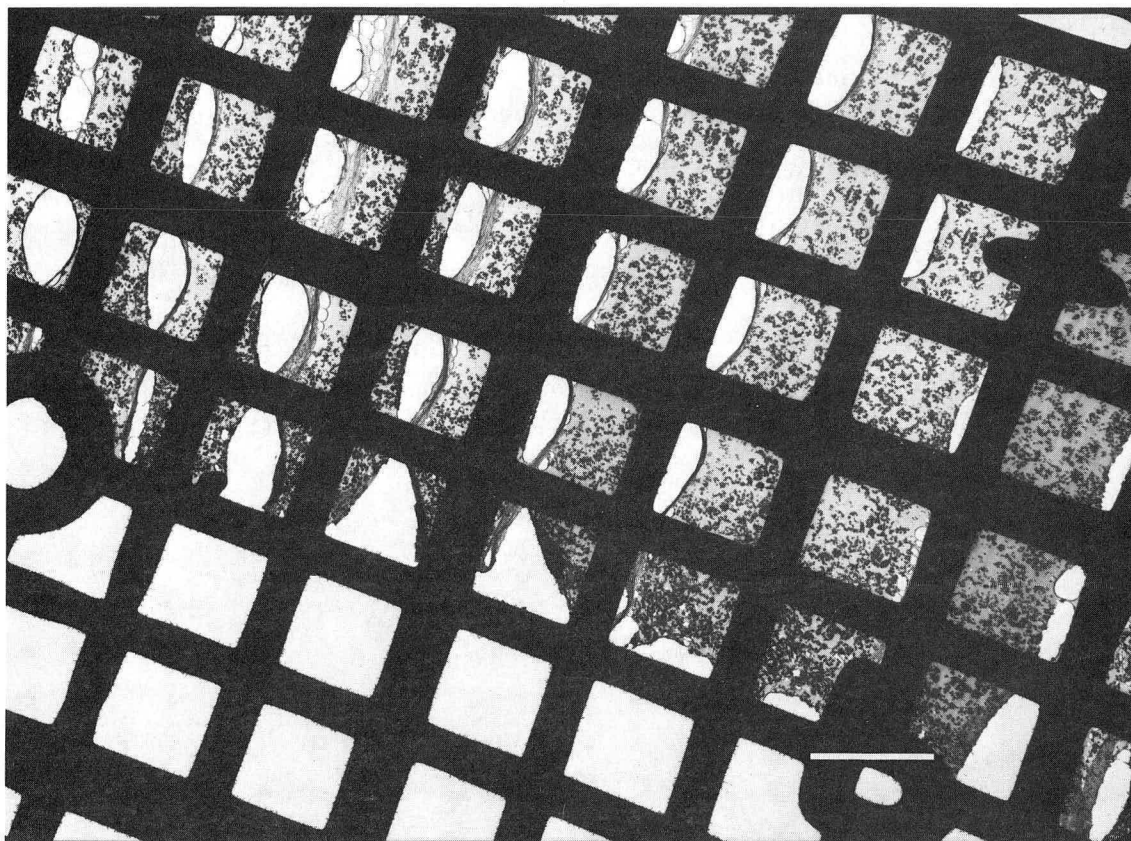
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Figure 2 - Microtomed thin section of a ferrisilicate analog of zeolite ZSM-5 embedded in LR White[®] resin.

Since microtomy involves cutting a series of sections through a particle or aggregate of particles, a single particle may be studied in a sequence of cuttings to reveal three dimensional information about the particle. Figure 3 shows a ribbon of microtomed sections of a ferrisilicate catalyst embedded in LR White[®] resin on a copper grid. One can easily identify particles that appear in five or more sections of the ribbon. By imaging or collecting spectra from the particles in each section, structural or compositional variations throughout the particles can be determined.

CONCLUSIONS

High quality TEM specimens of zeolites and other catalysts may be prepared



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Figure 3 - Ribbon of microtomed sections of a ferrisilicate analog of zeolite ZSM-5 embedded in LR White[®] resin on a copper grid. Bar = 50 μm .

with relative ease using microtomy. For hard ceramic catalysts, the acrylic embedding resin LR White[®] penetrates and binds to the particles and polymerizes to an equivalent hardness. Silver sections (60-90 nm thick) can be reproducibly cut and grey sections (\leq 50 nm thick) are possible when the diamond knife edge is new. Specimens prepared by microtomy are uniformly thin and well suited to high resolution imaging as well as analytical microscopy.

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