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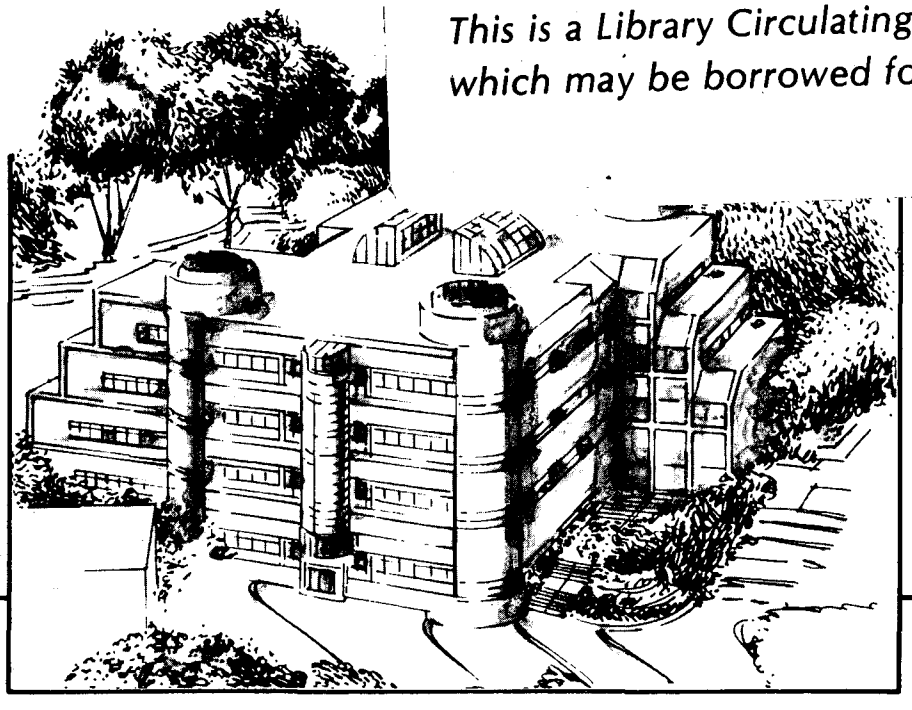

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MICROSTRUCTURAL STUDY OF AN IRON SILICATE CATALYST USING ELECTRON MICROSCOPY

By

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ABSTRACT

The effects of various synthesis conditions on the structure of iron silicate analogs of zeolite ZSM-5 were considered. Scanning electron microscopy (SEM) was used to determine the particle size distributions and morphologies. Particle sizes vary from tenths of a micron to several microns, depending on degree of agitation during crystal growth, while morphology is additionally dependent on the concentration of iron in the gel during crystallization. Transmission electron microscopy (TEM) was used to determine the size and spatial distributions of iron-rich second phase particles within the ZSM-5 framework as a function of SiO_2/Fe_2O_3-ratio, thermal and hydrothermal treatments.

INTRODUCTION

Iron silicate analogs of the zeolite ZSM-5 may be directly synthesized from iron silicate gels in a manner which differs slightly from the alumino-silicate ZSM-5 (1). The resultant

white, crystalline iron silicate is referred to as FeZSM-5 in the as-synthesized form. Thermal treatment removes the organic crystal-directing agent and moves some of the framework iron into non-framework sites producing the calcined form of the molecular sieve FeZSM-5 (2-4). Subsequent hydrothermal treatment moves more of the iron out of the molecular sieve framework (2-4). This iron-rich second phase and the ZSM-5 pore structure can be used to convert synthesis gas (CO and H_2) to "gasoline range" hydrocarbons and water (Fischer-Tropsch synthesis). To optimize the Fischer-Tropsch catalyst, homogeneity in the particle size distribution and in the distribution of catalytic iron throughout the particles is desired.

Electron microscopy, with its high spatial resolution, plays an important role in the physical characterization of these catalysts. Scanning electron microscopy (SEM) is used to characterize the molecular sieve particle sizes and morphologies as a function of preparation conditions. Transmission electron microscopy (TEM) is used to follow the changes in the microstructure of the iron silicates caused by different growth conditions and subsequent thermal and hydrothermal treatments.

SCANNING ELECTRON MICROSCOPY

The particle sizes and morphologies as a function of various preparatory conditions, thermal and hydrothermal treatments were studied using SEM. Samples of FeZSM-5 in the as-synthesized form showed marked differences in particle size as well as morphology depending on whether the gel was stirred or not stirred during crystallization. When the gel was stirred the particles were generally less than 1μm diameter and appeared to be spherical and "cauliflower-shaped" aggregates of smaller crystallites, see figure 1. Particles grown from unstirred gels varied in size as well as morphology, see figure 2. Most particles appeared to be 2-5μm diameter aggregates of smaller elementary crystallites; however, some single, twinned

and inter-grown crystals were observed.

Decreasing the iron concentration in the gel from $SiO_2/Fe_2O_3 \simeq 50$ to $SiO_2/Fe_2O_3 \simeq 200$ resulted in more spherical particle aggregates in the stirred samples and larger particle aggregates in the unstirred samples; in the unstirred batch some of the spherical particles were greater than 5 μm in diameter. Thermal and hydrothermal treatments did not change the size nor the morphology of the FeZSM-5 particles.

TRANSMISSION ELECTRON MICROSCOPY

Six samples grown from stirred and unstirred gels with SiO_2/Fe_2O_3-ratio = 50, 90 and 200 were studied with TEM before and after calcination and steam treatments. TEM specimens consisted of uniformly thin (50-80nm) sections of the iron silicate particles embedded in an acrylic resin; they were prepared by microtomy, described in detail elsewhere (5,6). Second phase iron-rich particles ($\leq$ 2.5 nm) were observed to form during thermal treatment and grow during subsequent steaming in all FeZSM-5 samples investigated (Fig. 3). The temperature of the hydrothermal treatment has a more pronounced effect on the second phase particle growth than does the duration of the treatment or the SiO_2/Fe_2O_3-ratio. For all stirred samples hydrothermally treated at 550 °C second phase particles ranged in size from 1.5 to 4 nm for steaming times of 1, 2 or 4 hours. However when treated at 700 °C for 4 hours, the particles ranged in size from 5 to 10 nm.

All molecular sieve particles grown from unstirred gels contained (6-15 nm) voids, some that were crystallographic, (Fig. 3). These voids appeared largely unchanged by heat and steam treatments. Steam treatments at 550 °C of the unstirred samples produced second phase particles, 2-6nm diameter, for times of 1, 2 or 4 hours. Treatment at 700 °C for 4 hours resulted in particles 7.5 to 14 nm in size. Hydrothermal treatment of unstirred samples con-

sistently resulted in larger second phase particles than did the same treatment to stirred samples. This could be due to a less homogeneous iron distribution in the as-synthesized form of the unstirred samples and/or enhanced diffusion during steam treatments, perhaps involving the voids.

The identity of the iron-rich second phase is currently being investigated. The particles larger than 7.5 nm are crystalline but electron diffraction is very weak and diffuse due to their small size. After prolonged electron beam exposure, the molecular sieve structure damages and becomes amorphous facilitating TEM images of the second phase particles (Fig. 4). Both fringe spacings and microdiffraction are being used to identify the particles.

CONCLUSIONS

SEM has shown that stirring the gel during crystal growth results in small (.5μm - 1μm) molecular sieve particle aggregates. Crystal growth without agitation produces some single crystals in addition to the micron or larger sized particle aggregates. In the stirred batches, the particle morphology changes from regular spheres to irregular spheres and cubes as the iron content increases; this is analogous to the effect of increasing the aluminum content in ZSM-5 zeolites.

TEM has shown that iron-rich second phase particles form and grow throughout the molecular sieve crystals during thermal and hydrothermal treatments of the iron silicate, FeZSM-5. The size of the second phase particles is strongly dependent on the temperature of the steam treatment and on whether the molecular sieve crystals were grown from stirred or unstirred gels. The largest second phase particles were observed in unstirred crystals steam treated at 700 °C.

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FIGURE CAPTIONS

Fig. 1--SEM image of iron silicate molecular sieve in the as-synthesized form, grown from a stirred gel with SiO_2/Fe_2O_3-ratio $\simeq$ 50. XBB 8711-10115

Fig. 2--SEM image of iron silicate molecular sieve in the as-synthesized form, grown from an unstirred gel with SiO_2/Fe_2O_3-ratio $\simeq$ 50. XBB 8711-10114

Fig. 3--FeZSM-5 particle aggregate after 4h steam treatment at 550 °C, SiO_2/Fe_2O_3-ratio = 50, unstirred gel. Voids, some crystallographic, are observed throughout the aggregate, as are second phase iron-rich particles (2 to 6 nm). XBB 882-1491

Fig. 4--Second phase particles (lattice fringes) in molecular sieve matrix, FeZSM-5, after 4h steam treatment at 700 °C, SiO_2/Fe_2O_3-ratio = 200. Molecular sieve structure looks amorphous due to electron beam damage. XBB 882-1492

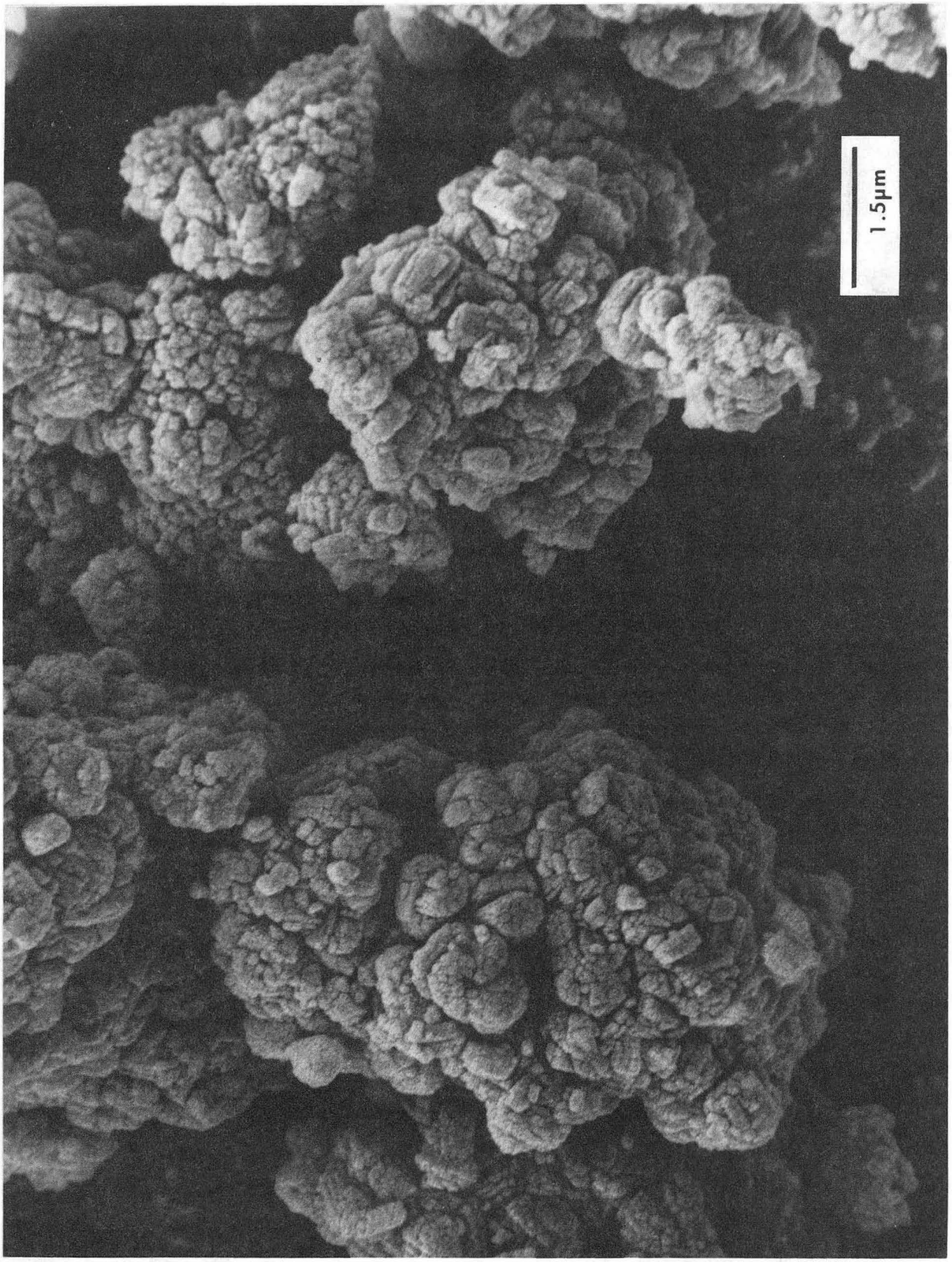

Figure 1

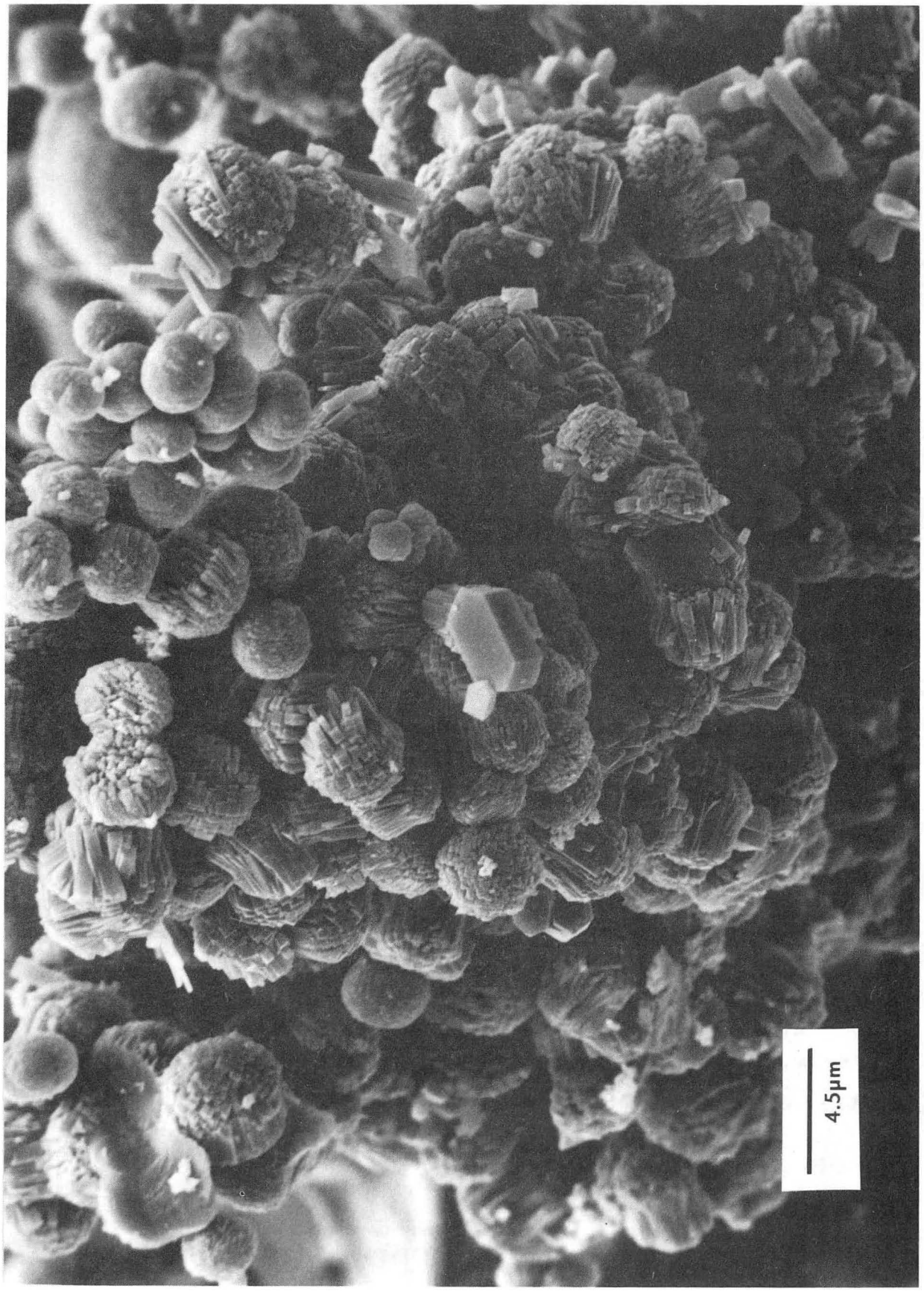

Figure 2

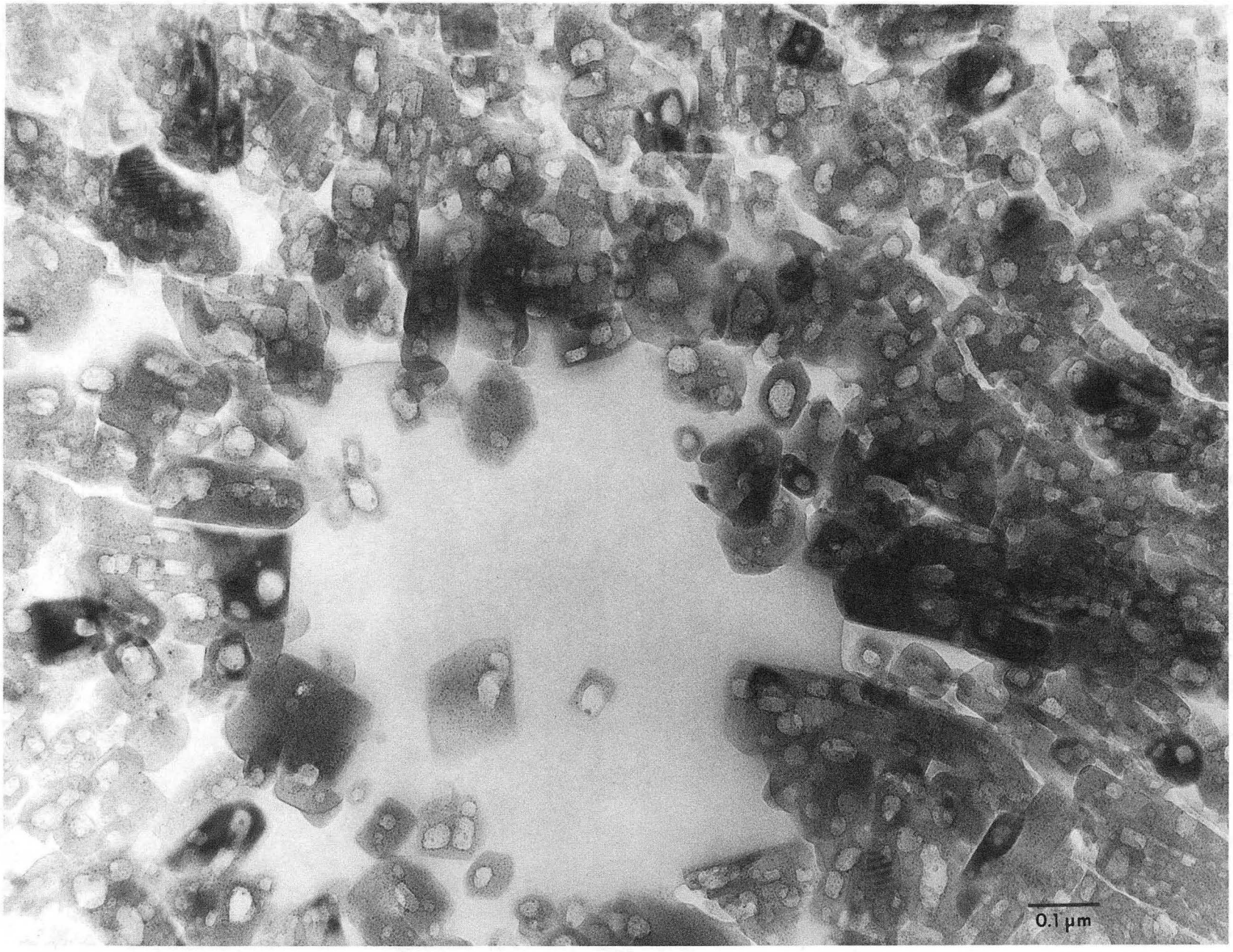

Figure 3

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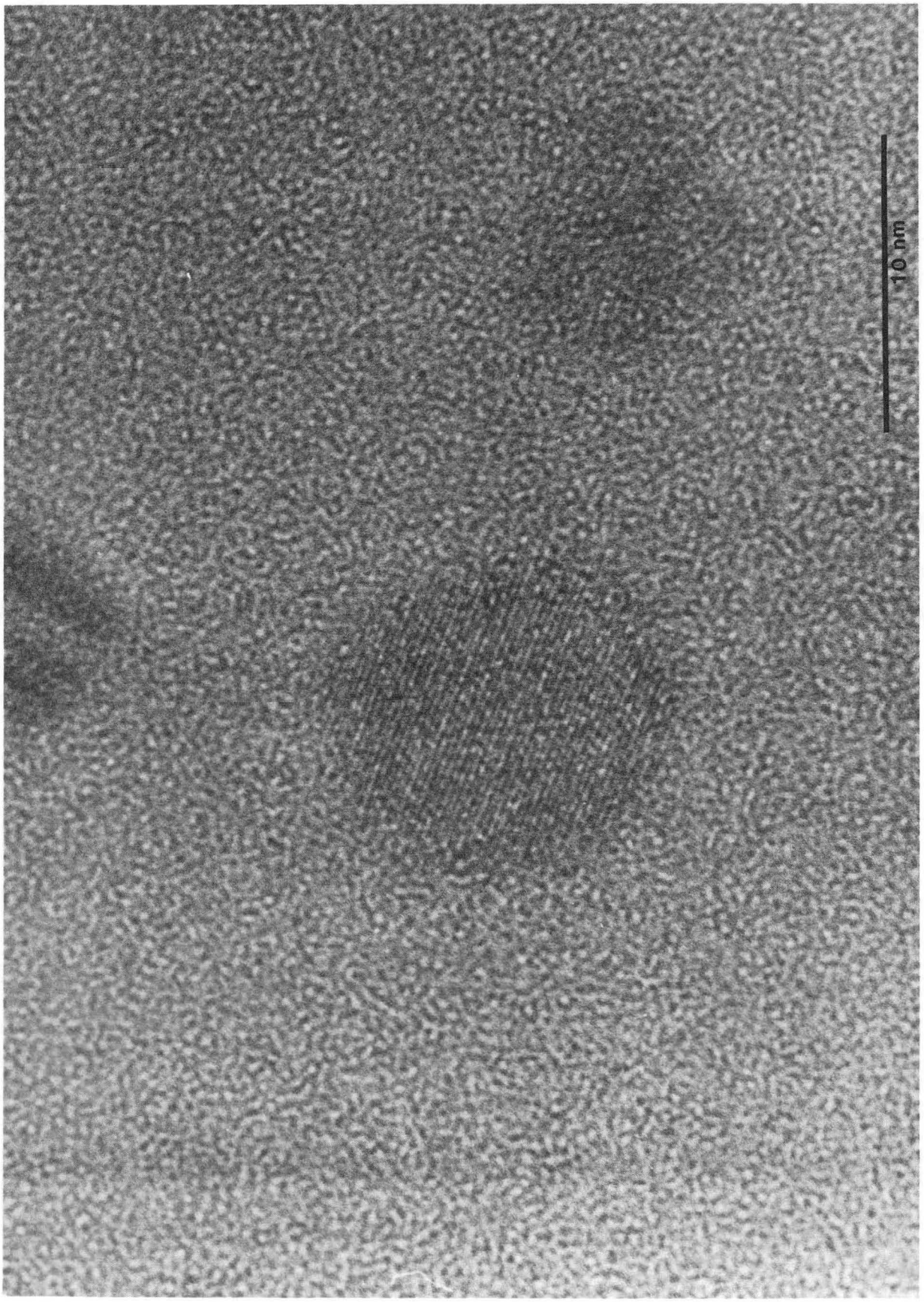

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Figure 4

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