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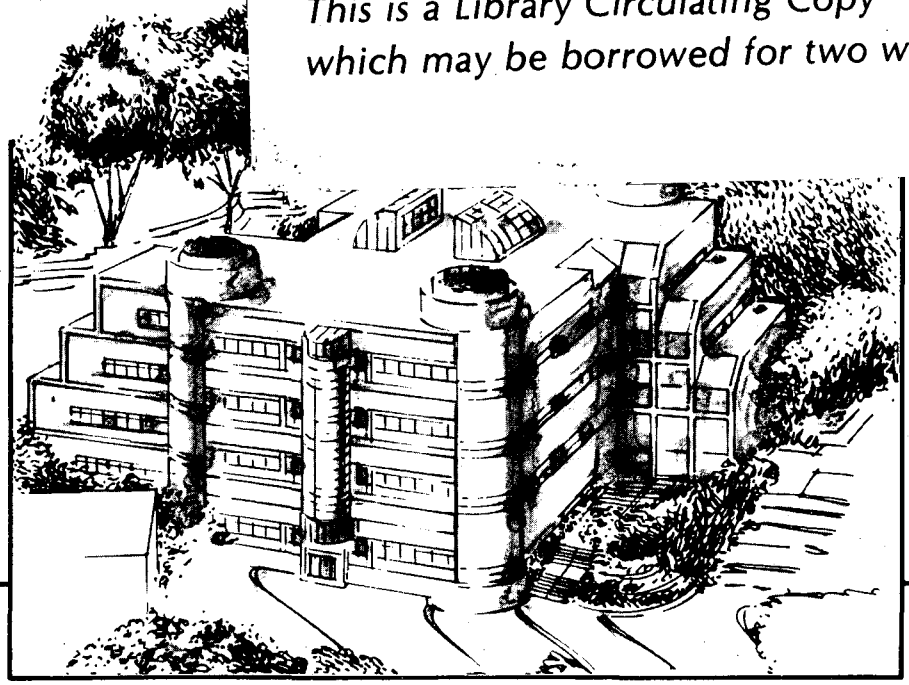

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MICROSTRUCTURAL EVOLUTION OF AN IRON SILICATE CATALYST WITH THERMAL AND HYDROTHERMAL TREATMENTS

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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.

Scanning electron microscopy (SEM) was used to characterize the overall molecular sieve particle sizes and morphologies as a function of preparation conditions. When the gel was stirred during crystallization the particles were generally less than 1μm diameter and appeared to be "cauliflower-shaped" aggregates of smaller crystallites. Particles grown from unstirred gels varied in size as well as morphology. Most particles appeared to be 2-5μm diameter aggregates of smaller elementary crystallites; however, some single, twinned and inter-grown crystals were observed. SEM images of thermally and hydrothermally treated forms of the molecular sieves showed them to be identical in size and morphology to the as-synthesized forms.

Transmission electron microscopy (TEM) was used to follow the microstructural changes in the iron silicate molecular sieve as a function of synthesis and treatment conditions. 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] Second phase iron-rich particles ($\leq$ 2.5 nm) form during thermal treatment and grow during subsequent steaming in all samples investigated (Fig. 1). The temperature of the hydrothermal treatment has a more pronounced effect on the particle growth than does the duration of the treatment. For 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 h. However when treated at 700 °C for 4 h, the particles ranged in size from 5 to 10 nm. The second phase particles appear throughout the aggregate but are often clustered near the edges of the individual crystallites within the agglomerate.

Unstirred gels result in molecular sieve particles containing (6-15 nm) voids, many that are crystallographic; these voids are largely unaffected by steam treatments (Fig. 1). Hydrothermal treatment at 550 °C of unstirred samples produced 2 to 6nm second phase particles for steaming times of 1, 2 or 4 h; and treatment at 700 °C for 4 h resulted in 7.5 to 14nm particles. The larger second phase particles in unstirred samples are probably due to enhanced diffusion as compared to the stirred samples, this might be a result of the voids in the unstirred samples.

The identity of the iron-rich second phase is currently being investigated. The particles larger than 7.5 nm are crystalline but diffraction is very weak compared to that from the ZSM-5 structure. After prolonged electron beam exposure, the molecular sieve structure damages and looks amorphous in TEM images yielding reasonable images of the second phase particles, (Fig. 2). The fringe spacings and microdiffraction are being used to identify the particles.[6]

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6. Sincere gratitude is expressed toward my thesis advisor Prof. R. Gronsky, and to Prof. C.E. Lyman, Dr. V. Nair and Dr. R. Szostak for stimulating discussions and support. This work has been supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC03-76SF00098.

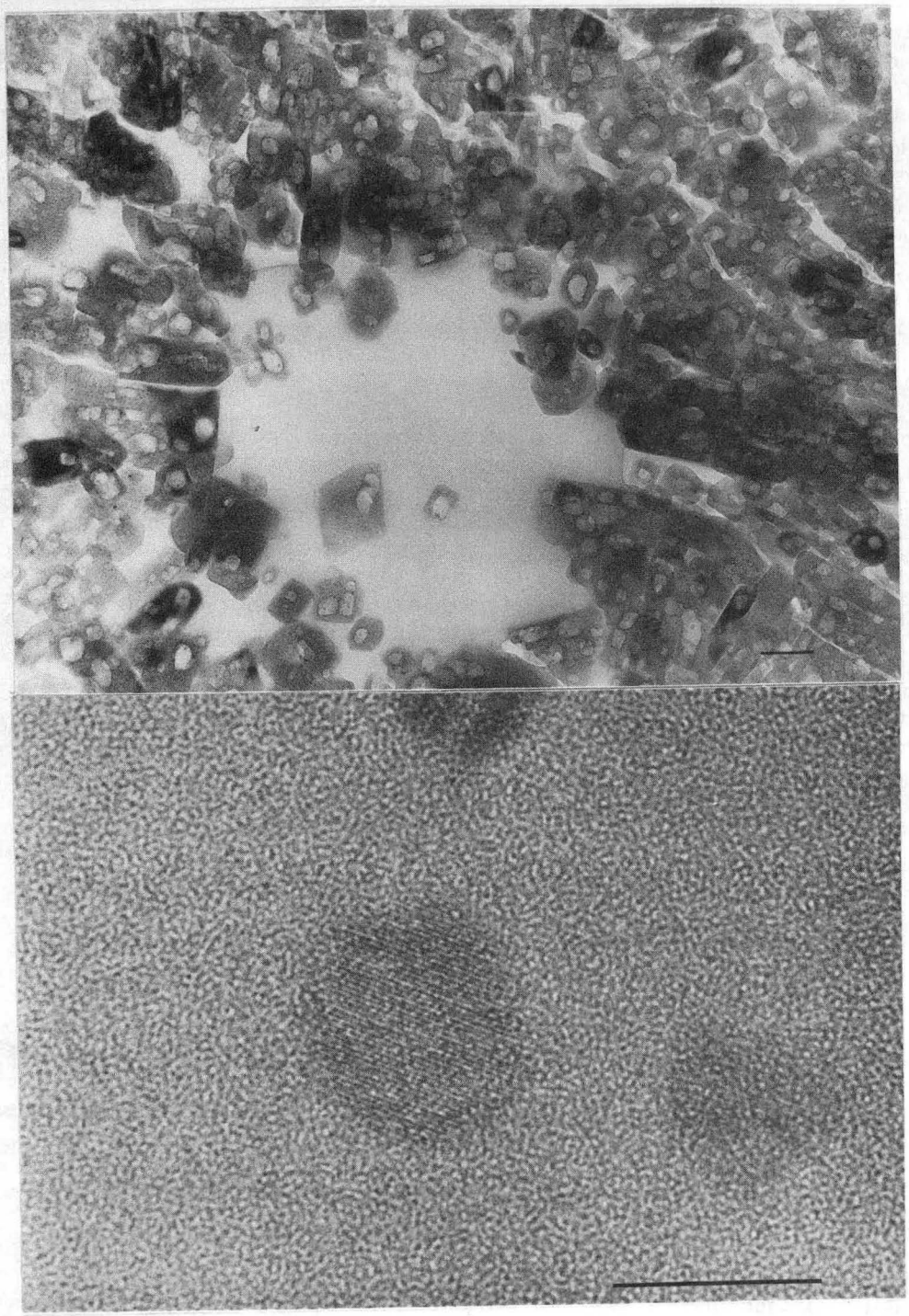

FIG. 1--FeZSM-5 particle aggregate after 4h steam treatment at 550 °C, Si/Fe-ratio = 25, unstirred gel. Voids, many crystallographic, are observed throughout the aggregate, as are second phase iron-rich particles (2 to 6 nm). Bar = 0.1 μm. XBB 882-1491

FIG. 2--Second phase particles (lattice fringes) in molecular sieve matrix, FeZSM-5 after 4h steam treatment at 700 °C, Si/Fe-ratio = 88. Molecular sieve structure looks amorphous due to electron beam damage. Bar = 10 nm. XBB 882-1492

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