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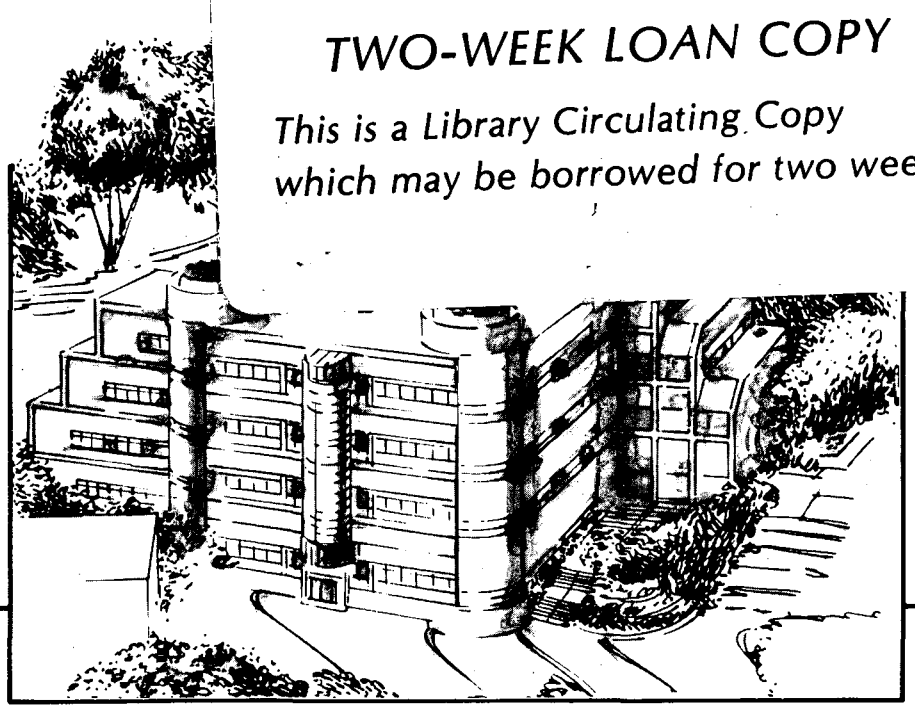

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# X-RAY EMISSION SPECTROSCOPY STUDY OF IRON SILICATE CATALYST FeZSM-5

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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] Homogeneity in the distribution of catalytic iron throughout the particles is desired in an optimal catalyst. Distribution of the iron throughout the framework in the as-synthesized forms would affect the final distribution of catalytic iron in the calcined and steamed forms; thus, the iron distribution throughout the as-synthesized and calcined forms of FeZSM-5 were studied using the high spatial resolution of the analytical electron microscope.

X-ray emission spectroscopy (XES) performed in the transmission electron microscope (TEM) and the scanning transmission electron microscope (STEM) was used to determine the inter- and intra-particle composition variations for FeZSM-5. For the purposes of this discussion, the word "particle" is used to describe the particle agglomerates not the individual crystallites making up the agglomerate, as shown in Fig. 1. The effects of gel iron concentration, stirring during crystallization, particle size, as well as thermal treatment were considered. Specimens consisted of uniformly thin (90-100nm) sections of the iron silicate particles embedded in an acrylic resin (Fig. 1).[5] These microtomed specimens met the thin-film conditions for XES (<150nm), thus absorption and fluorescence corrections were neglected.[6]

Energy dispersive x-ray spectra (EDS) of all FeZSM-5 samples showed silicon and iron peaks corresponding to the iron silicate molecular sieve particles, and copper peaks resulting from the copper support grids. Spectra collected using the Vacuum Generators HB-501 STEM equipped with a Link Analytical windowless x-ray detector also showed oxygen and carbon peaks corresponding to the catalyst and the carbon coating (applied to prevent charging) (Fig. 2). In some spectra, a small chromium peak was observed; this was probably due to a small amount of chromium contamination from the stainless steel crystallization vessel.

In the TEM, XES has shown that the Si/Fe-ratio of the as-synthesized FeZSM-5 particle aggregates is independent of particle size and stirring, although the homogeneity of the inter-particle iron distribution does improve slightly with stirring. As expected, thermal treatments do not significantly change the average Si/Fe-ratios of the FeZSM-5; however, the particle to particle variations do increase, particularly in very low iron samples.

Line profiles obtained in the STEM of 150nm wide calcined FeZSM-5 particles stirred during crystallization, showed that areas of very high iron concentration appear most frequently near the particle edges (Fig. 3). This suggests that iron migrates to and agglomerates on the surface during calcination.

Line profiles and spectra of calcined FeZSM-5, grown without stirring show increased iron concentration at the center of the particle agglomerate as compared to the agglomerate edges. This concentration gradient might be the result of enhanced iron incorporation during crystal nucleation, while continued crystal growth may occur from an iron-depleted gel.[7]

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7. The assistance of Dr. J.R. Michael and the Bethlehem Steel Corporation, Dr. R. Szostak and Dr. V.

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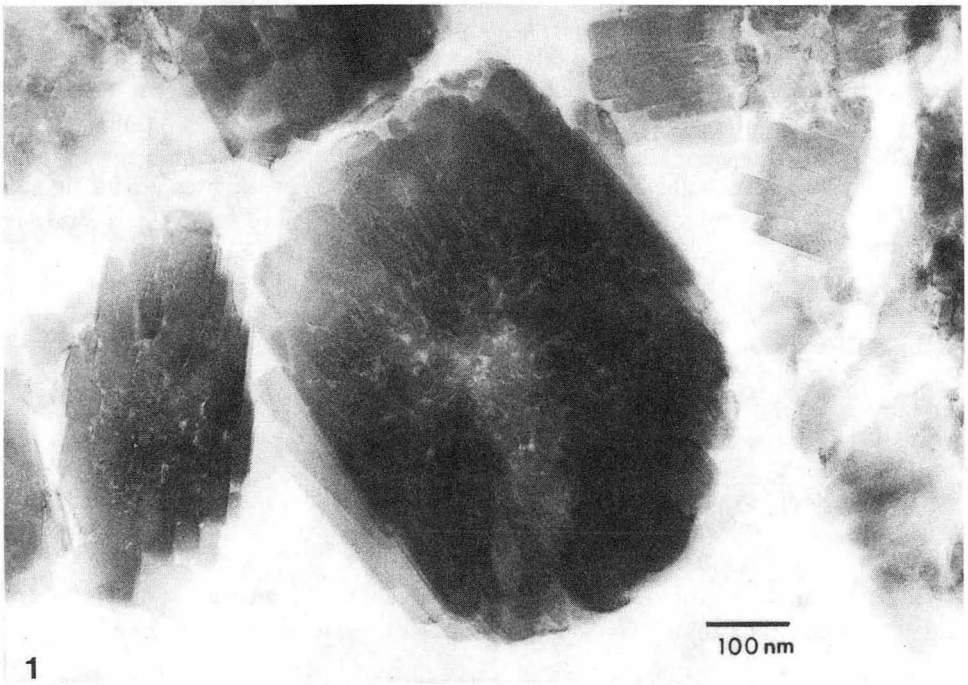


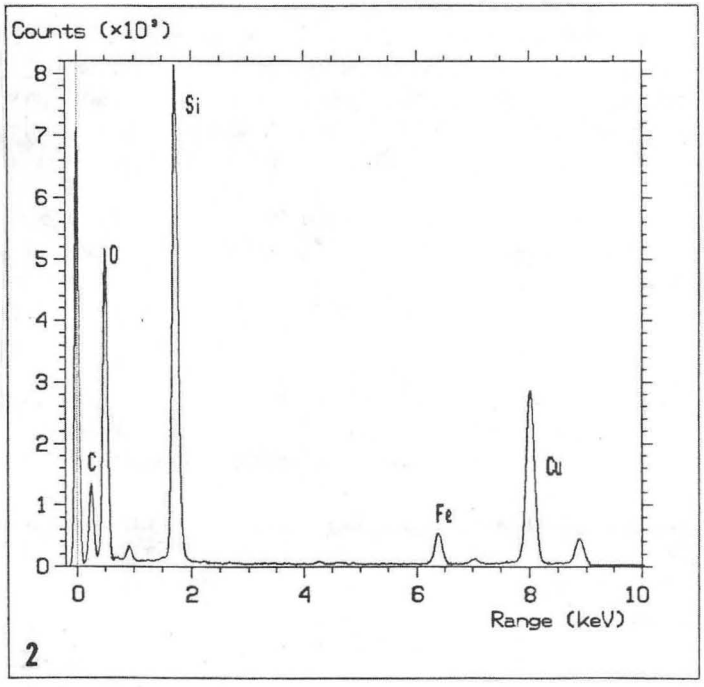


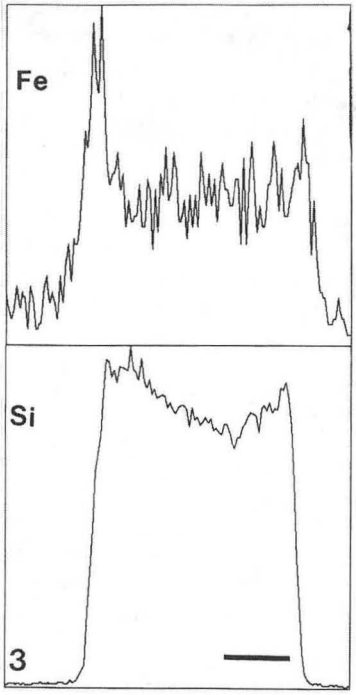


FIG. 1-TEM image of microtomed thin section of stirred, as-synthesized FeZSM-5, embedded in acrylic resin. Bar = 100 nm. XBB 870-9599

FIG. 2-Representative x-ray spectrum taken on HB-501 STEM from calcined FeZSM-5 grown from unstirred gel with Si/Fe≃25. XBL 883-696

FIG. 3-Iron and silicon line profiles through stirred, calcined FeZSM-5 particle (Si/Fe≃25), showing high iron concentration near edge. Bar = 50 nm. XBL 883-697

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