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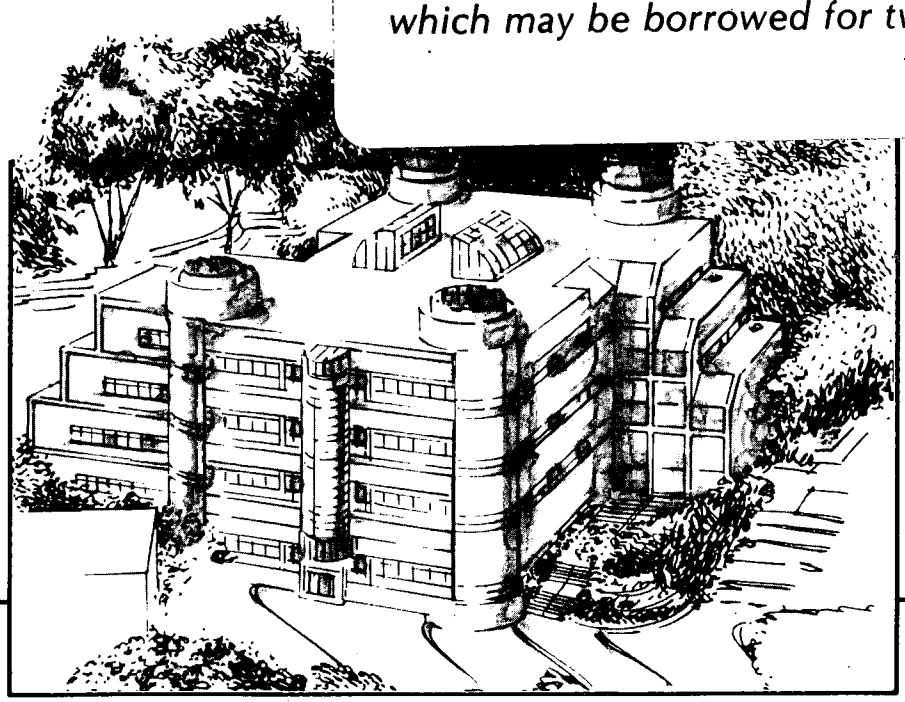

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ELECTRON MICROSCOPY STUDY OF MORPHOLOGY AND COMPOSITION OF A FERRISILICATE CATALYST

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ABSTRACT

The effects of various synthesis conditions on the structure and composition of ferrisilicate analogs of zeolite ZSM-5 were considered. Scanning electron microscopy (SEM) was used to determine the particles 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.

X-ray emissive spectroscopy (XES) performed in the transmission electron microscope (TEM) was used to determine their composition variation. The distribution of iron amongst the crystals is more homogeneous if the gel is stirred and it does not depend on particle size.

INTRODUCTION

Iron supported on silica or alumina is an active, flexible catalyst for the conversion of synthesis gas (CO and H_2) to hydrocarbons and water (Fischer-Tropsch synthesis) [1]. In the late 1970's, researchers at Mobil synthesized a shape selective zeolite, ZSM-5, that was excellent for converting methanol to "gasoline range" hydrocarbons with high yield [2,3]. Mobil researchers also tested the ability of the ZSM-5 to control the products of the Fischer-Tropsch reaction by reacting CO and H_2 over the physical mixture of catalytically active iron and ZSM-5 powder [4, 5]. The results were very promising. Throughout the eighties, researchers worldwide have been trying to optimize the distribution of Fe *inside* the ZSM-5 channels to produce a better Fischer-Tropsch catalyst [6-9].

Ferrisilicate analogs of the ZSM-5 zeolite may be directly synthesized from ferrisilicate gels in a manner which differs slightly from the alumino-silicate ZSM-5 [9]. The resultant white, crystalline ferrisilicate 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 [10- 12]. Subsequent hydrothermal treatment moves more of the iron out of the molecular sieve framework [10-12]. This second iron oxide phase can then be on the surface or inside the pores of the ZSM-5 structure.

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. X-ray emissive spectroscopy (XES) performed in the

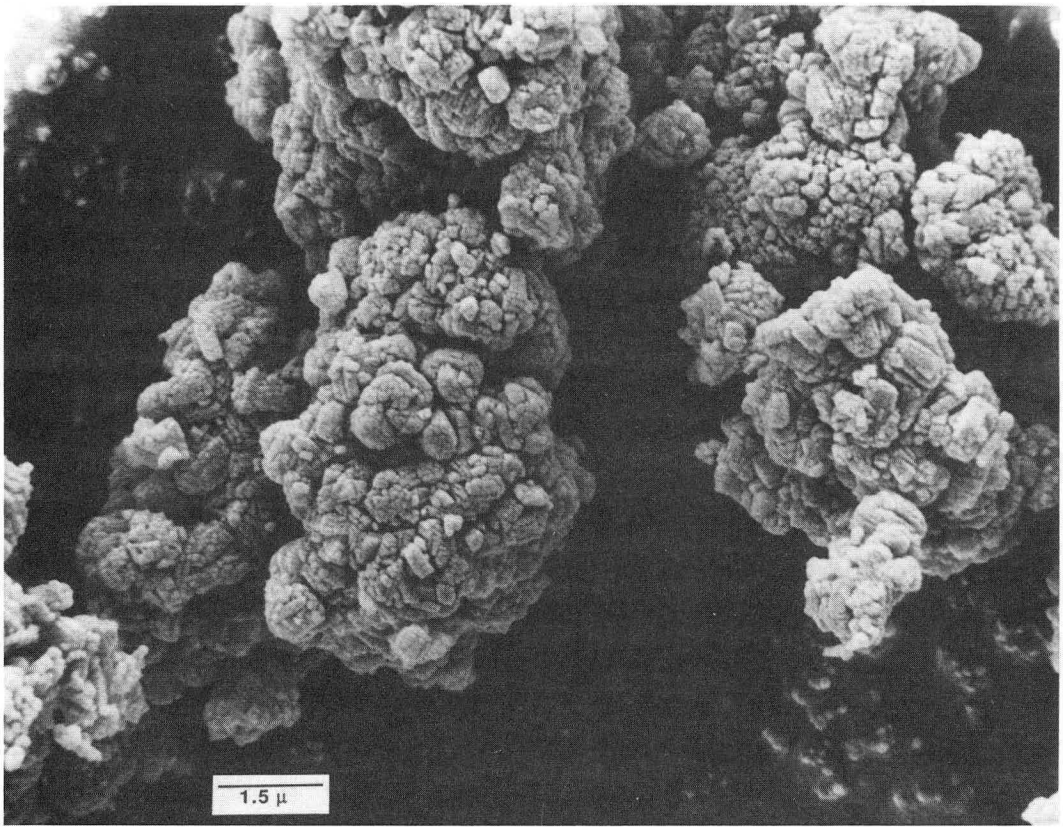

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Figure 1 - SEM image of ferrisilicate molecular sieve in the as-synthesized form, grown from a stirred gel with Si/Fe-ratio $\simeq$ 25.

transmission electron microscope (TEM) is used to determine the inter-particle composition variation (i.e., Si/Fe) of the ferrisilicates.

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 complex-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 Si/Fe $\simeq$ 25 to Si/Fe $\simeq$ 100 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. Images of thermally and hydrothermally treated forms of the molecular sieves were identical in size and morphology to the as-synthesized forms.

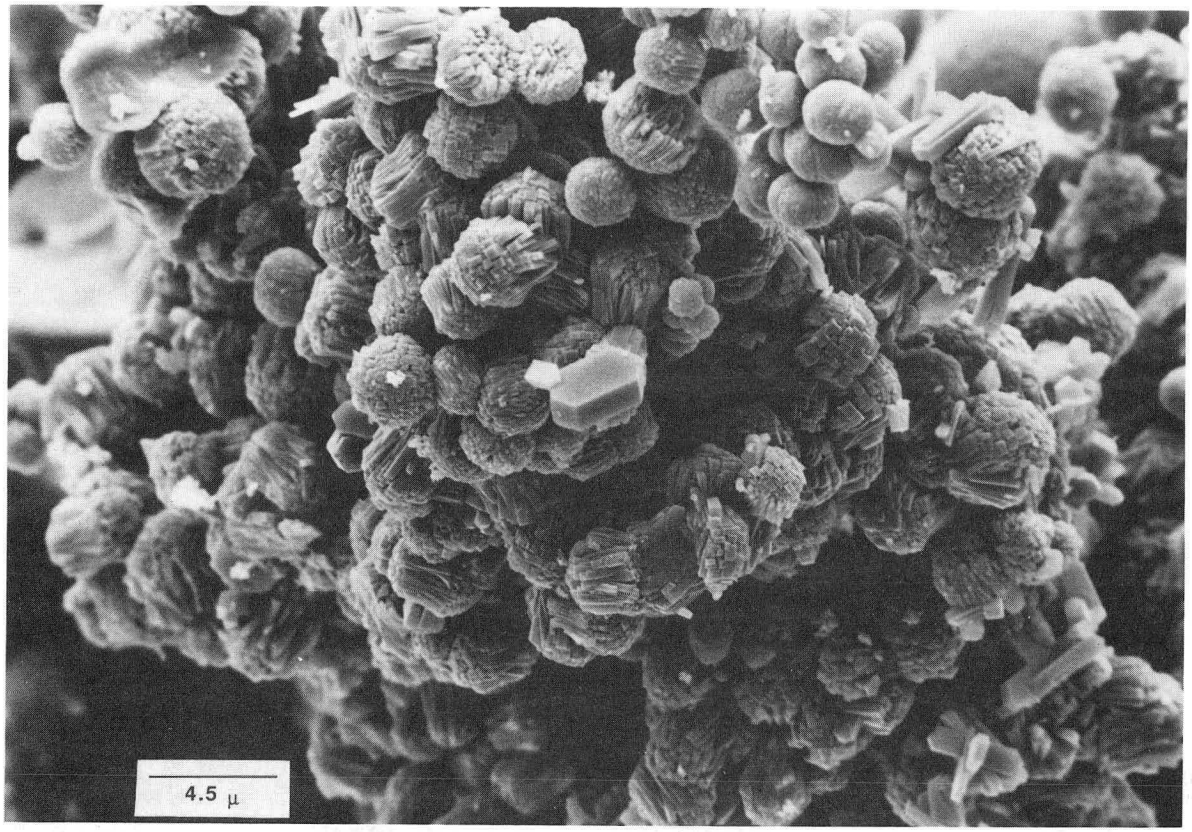

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Figure 2 - SEM image of ferrisilicate molecular sieve in the as-synthesized form, grown from an unstirred gel with Si/Fe-ratio $\simeq$ 25.

X-RAY EMISSIVE SPECTROSCOPY

The inter-particle iron distribution in the ferrisilicate molecular sieves has been studied using X-ray emissive spectroscopy in the transmission electron microscope. For the purposes of this discussion, the word "particle" is used to describe the particle aggregates shown in figure 3, not to describe the individual crystallites making up the agglomerate. The effects of gel iron concentration, stirring during crystallization, particle size, as well as thermal treatment were considered. The stirred samples were in the as-synthesized and calcined forms and had Si/Fe-ratios $\simeq$ 25, 50 and 100; the unstirred samples were in the as-synthesized and calcined forms and had Si/Fe-ratio $\simeq$ 25. The Si/Fe-ratios were determined by atomic absorption spectroscopy and closely matched the Si/Fe-ratio of the gel. TEM specimens consisted of thin sections of the ferrisilicate particles embedded in an acrylic resin, (figure 3); they are prepared by microtomy, described in detail elsewhere [13]. Experiments were carried out in a Phillips 400T TEM/STEM operated at 100kV accelerating voltage. X-rays were detected with a Kevex, beryllium-window, X-ray detector; spectra were collected for 300 seconds, (livetime) to minimize statistical counting uncertainty. Probes were formed, as best possible, to equal the size of the particle probed without illuminating adjacent particles. This choice of probe size could, at times, have resulted in under-sampling of the particle edges. This would result in an incorrect assessment of the inter-particle iron distribution only if the iron concentration at the edges of a particle differed greatly from its internal concentration. Work is in progress to address this question; preliminary results indicate that it is not a significant effect.

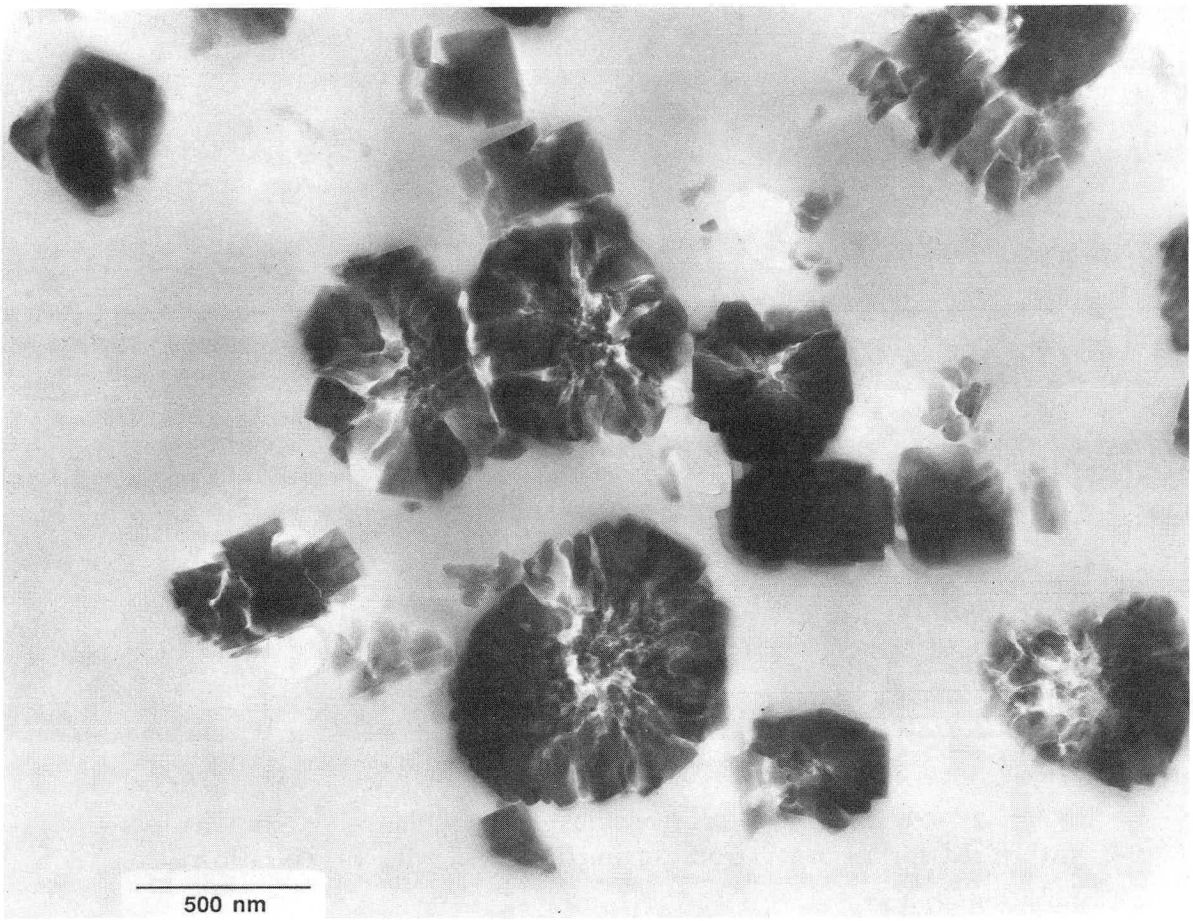

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Figure 3 - TEM image of microtomed thin section of as-synthesized FeZSM-5, embedded in an acrylic resin. The ferrisilicate was grown from a stirred gel with Si/Fe-ratio $\simeq$ 100.

Energy dispersive X-ray spectra (EDS) of all FeZSM-5 samples showed silicon and iron peaks corresponding to the ferrisilicate molecular sieve particles, and copper peaks resulting from the copper support grids. 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.

On average, 20 spectra from various particles were collected for each sample; this was to insure that the spectra were representative of the bulk samples. For each spectrum, a "hand-fit" background was subtracted and the total number of X-ray counts in 200 eV wide windows for silicon and iron were recorded. The number of the counts in the silicon window divided by the number of counts in the iron window was taken as the Si/Fe-ratio for this study. In the near future, this relative measure of Si/Fe-ratio will be converted to actual Si/Fe-ratios by calibration of the X-ray detector for oxides containing silicon and iron. Currently, the numerical values of Si/Fe-ratios, determined by XES, are artificial in that they do not correspond to those determined by the atomic absorption, however their relative values are important and are used in the present study.

A summary of the relative Si/Fe-ratios and their percent standard deviations is shown in table I. In this case, the standard deviation is used as a measure of the spread in the data points for the given sample.

Table I - Si/Fe-ratios for various FeZSM-5 samples.			
Form	Si/Fe-ratio by AA	Relative Si/Fe-ratio by XES	percent std. dev.
stirred, as-synthesized	27	16.6	4.2
calcined		16.2	7.4
stirred, as-synthesized	46	27.2	4.4
calcined		26.0	10.
stirred, as-synthesized	88	50.2	16.
calcined		51.2	48.
unstirred, as-synthesized	25†	16.8	20.
calcined		12.0	18.
† Si/Fe-ratio of the gel, not measured by AA.			

The Si/Fe-ratio of FeZSM-5 increases as the concentration of iron in the crystallizing gel decreases; this is in agreement with the atomic absorption measurements. The effect of particle size on the distribution of iron among the FeZSM-5 particles can be seen best by comparing the as-synthesized, stirred and unstirred samples. As stated above, the particle sizes of the stirred samples are 1 μm or less, while in the unstirred samples, particle diameters are greater than 1 μm. The Si/Fe-ratios measured by XES for both the stirred and unstirred samples of FeZSM-5 are the same, thus it can be concluded that the distribution of iron is independent of particle size. Although the average Si/Fe-ratios are equal, the spread of the data is larger in the unstirred sample, indicating a more homogeneous distribution of iron with stirring during crystallization.

For all stirred samples, thermal treatment does not change the average Si/Fe-ratio, within a standard deviation. The particle-to-particle variations are larger as indicated by the increase in percent standard deviation; this suggests that there may be iron migration occurring during thermal treatment. In the case of the unstirred sample, there appears to be an increase in iron concentration with heat treatment; work is in progress to determine if this is generally true or an anomaly.

In the sample with the very high Si/Fe-ratio, stirring does not insure homogeneity of the inter-particle iron concentration. For the very low iron ferrisilicate, the spread in the data is three and one half times that of the samples containing moderate and high iron levels, indicating less homogeneity of iron distribution. Thermal treatment of the high Si/Fe-ratio sample results in greater inhomogeneity of the iron distribution amongst the particles, as compared to the other samples. This enhanced inhomogeneity could possibly be due to easier migration of some of the iron to the particle surfaces during heat treatment, for samples with very low iron concentrations. In samples with higher iron concentrations, a second iron oxide phase may form inside the ZSM-5 particles and reduce the migration of the iron to the outside of the particle.

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.

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.

ACKNOWLEDGMENTS

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