

TITLE: Modified Ferrisilicates for Syn-Gas Conversion:
Impact of Ultra-high dispersion on Conversion

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OBJECTIVE: To identify high dispersion iron oxide/molecular sieve catalysts prepared from ferrisilicate molecular sieves and test their ability to convert H_2/CO to liquid fuel products.

ABSTRACT

Modified ferrisilicate catalysts can be activated for use in the conversion of syn-gas to liquid fuel products. Through detailed characterization of the new modified ferrisilicate materials, correlations can ultimately be drawn between the location of the iron and the degree of dispersion with its catalytic activity. Ultra-high dispersion iron oxide within the pores of the ZSM-5 molecular sieve structure can be uniquely prepared through selective thermal and hydrothermal treatment of the single phase ferrisilicate molecular sieve. After careful characterization, samples containing SiO_2/Fe_2O_3 ratios of 90 which had been thermally ($550^\circ C$) and hydrothermally ($550^\circ C$, 1 hr, 100% steam) were chosen as characterization techniques employed indicated they contained significantly high dispersions of the iron oxide within the channels and minimum migration to, or presence of, surface iron on the crystals. Changes in product distribution, when these catalysts were tested for syn-gas activity were observed. Presence of carbon numbers C_2 and higher were directly dependent on the modification method used to prepare the initial iron oxide/molecular sieve catalysts. Olefinic products formed preferentially over the steamed catalyst while the more acidic thermally treated material produced higher carbon number and more paraffinic products.

METALLOSILICATE MOLECULAR SIEVES

The substitution of other elements for framework aluminum in the molecular sieve zeolites has provided an alternative means of modifying the acid properties [1-3]. However, framework substitution of the elements containing catalytically active oxide forms followed by post-synthesis modification provides a unique method for generating high dispersions of that catalytically active metal oxide within the pores and channels of the molecular sieve

structure [4-10]. Such a catalyst exhibits characteristic properties of the active metal oxide phase as well as the shape selective properties identified with the molecular sieve structure.

In this program we have examined the modification of pure single phase ferrisilicate molecular sieves with the ZSM-5 structure using a combination of thermal and hydrothermal treatment to develop a high dispersion iron oxide/molecular sieve syn-gas catalyst. Hydrothermal treatment is known to encourage loss of structural aluminum in the zeolite molecular sieves and similar loss has also been observed in the ferrisilicates materials. Unlike the aluminosilicates, nonframework iron oxide can be directly examined using magnetic measurements, EPR and Mossbauer spectroscopy. In addition, the sizable mass difference between the iron oxide and the silicate matrix allows one to readily examine the location and follow the migration of small particles of iron oxide within the highly silicious crystal using high resolution transmission electron microscopy. Two modified iron silicate catalysts were then examined for their effectiveness as a syn-gas conversion catalyst.

EXPERIMENTAL PROCEDURE

The synthesis procedures used for the preparation of the iron silicate analogs of zeolite ZSM-5 as well as the thermal and hydrothermal treatment of these materials and syn-gas reactor conditions have been described in detail elsewhere [7,8,11]. The notation used in this paper to represent the iron silicate materials with varying $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios is: Fe(xx) where (xx) is the bulk $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio of the sample as obtained from atomic absorption. Thus Fe(98) is the iron silicate with the ZSM-5 structure and a bulk $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratio of 98.

The as-synthesized iron silicates lack color while developing their characteristic iron-oxide color during the various treatments. Shown in Table 1 are the colors of the iron silicate and modified iron silicate materials after the modification procedure described. The method of preparation of the parent iron silicate was also found to change the nature of the resulting catalyst. Table 2 provides the comparison of catalyst samples prepared from samples of iron silicate which were crystallized in stirred and unstirred autoclaves. The difference in color as well as resultant properties were initially utilized in identifying and selecting appropriate catalysts for the syn-gas reaction.

Table 1: Colors of the iron silicate and modified iron silicate molecular sieve catalysts.

Sample Name	Color of Samples				
	As-synthesized	Calcined	Hydrothermally treated at 550°C		
			1 hour	4 hours	4 hours
Fe(175) & Fe(171)	White	White	Light Brown	Brown	Brown
Fe(92)	White	White	Light Brown	Dark Brown	Reddish Brown
Fe(54) & Fe(51)	White	Off-White	Brown	Dark Brown	Reddish Brown
Fe(24)	White	Brown		Reddish Brown	

Table 2: Comparison of colors of iron silicate catalysts which were prepared using stirred and unstirred crystallizing autoclaves.

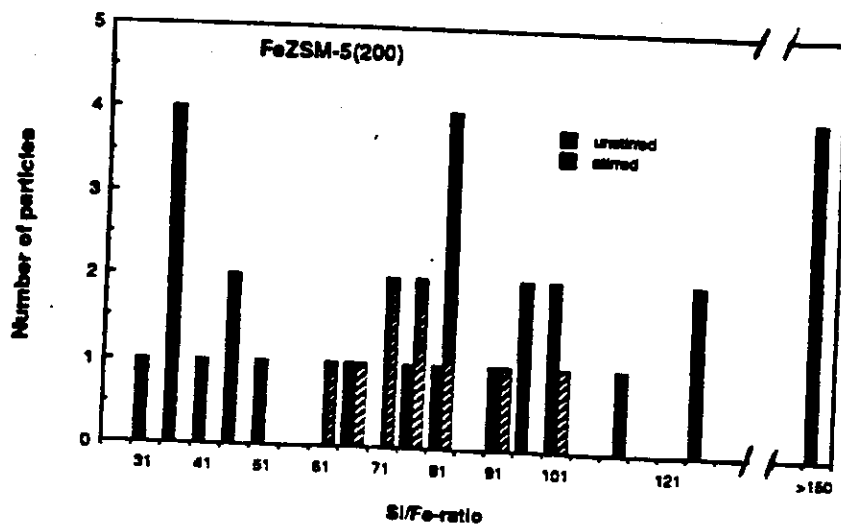
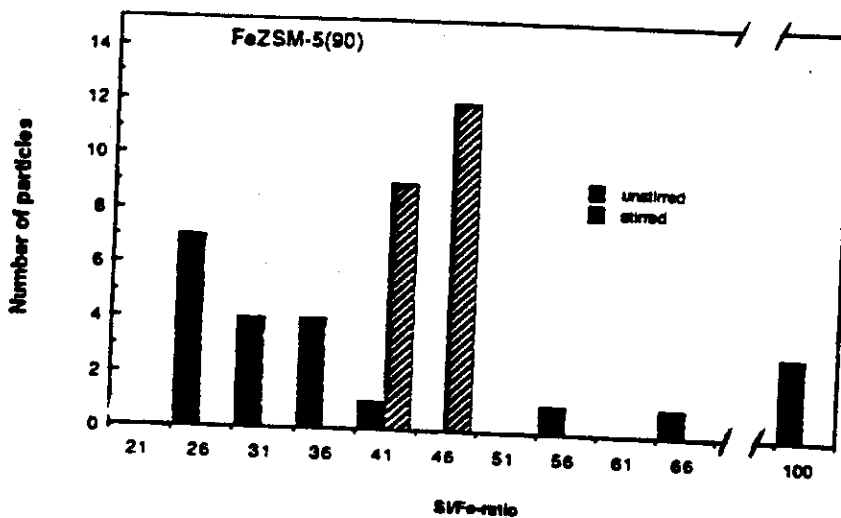
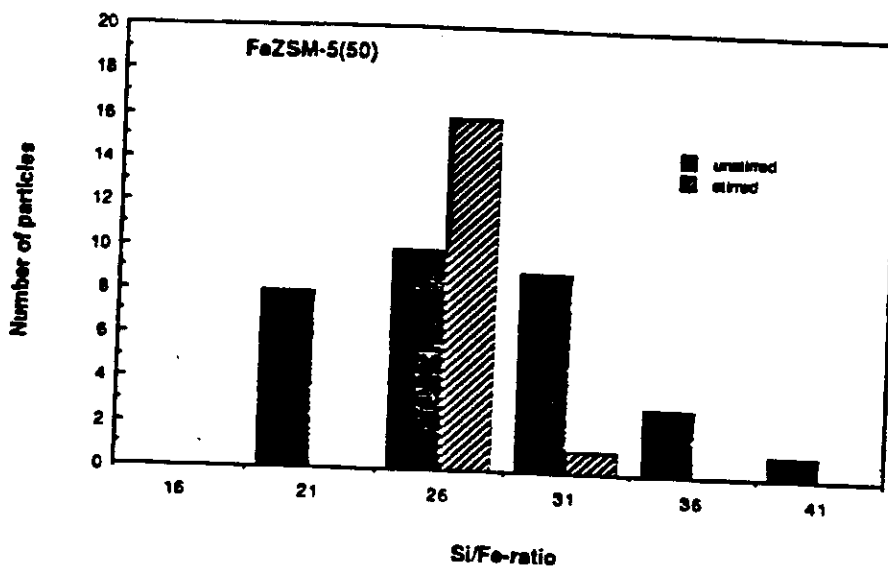
Sample Name	Color of the Materials		
	As-synthesized	Calcined	Hydrothermally treated at 550°C for 4 hours
Fe(92) Stirred	White	White	Brown
Fe(98) Un-Stirred	White	Off-White	Brown

EFFECT OF FERRISILICATE PREPARATION METHODS ON IRON HOMOGENEITY

A potential problem discovered early in our investigations was the dependence of iron dispersement homogeneously throughout the crystals on the utilization of a stirred or static autoclave crystallization system. Evenness in iron distribution was determined using the compositional analysis capability available on the transmission electron microscope. Crystallization of the FeZSM-5 crystals appears to decrease in homogeneity with increasing SiO₂/Fe₂O₃ ratio but overall crystallization utilizing the stirred autoclave produced the best compositionally invariant

product. A comparison between crystals obtained from a stirred crystallizer and an unstirred crystallizer at selected $\text{SiO}_2/\text{Fe}_2\text{O}_3$ ratios are shown in Figure 1. It was determined that the most suitable preparation method for the ferrisilicates was crystallization in a stirred autoclave vessel.

FIGURE 1



DETERMINING FRAMEWORK AND NON-FRAMEWORK IRON

The first step in identifying a viable modified iron silicate catalyst is to determine the extent of framework iron removal after the various thermal and hydrothermal treatments. This was accomplished using both compositional analysis and Mossbauer spectroscopic techniques. Selected results of this study comparing the two methods and showing excellent agreement in results are provided in Table 3 below.

Table 3. Comparison of the amount of tetrahedral iron as determined using compositional analysis and Mossbauer Spectroscopy.

Sample Name	Sample Description	% Iron present in tetrahedral framework sites using	
		Comp. Analysis ^a	Mossbauer ^b
Fe(171)	As-synthesized		100
	Calcined	97	95
	Steamed 4 hours at 550°C	46	35
Fe(51)	Calcined	40	45
	Steamed 4 hours at 550°C	15	10
Fe(24)	Steamed 8 hours at 550°C	0	8

COMPOSITION VARIATION ACROSS A PARTICLE OF FeZSM-5

The spherical ferrisilicate particles crystallized from the stirred autoclave were composed of clusters of much smaller crystallites. The spheres were sectioned and analysis taken at points at the edge and near the center of the sphere to determine the homogeneity of iron within the individual particles. The center of the spheres appeared less dense than the outer shell and contained a greater concentration of iron than the crystallites near the surface of the sphere. The results observed suggest that the nucleation of more iron rich crystallites is preferred at the onset of crystallization with subsequent crystallization of high silica containing material. Detailed examination of the process of iron silicate molecular sieve crystal growth was not pursued in this study.

SIZE AND LOCATION OF NON-FRAMEWORK IRON

Due to the significant difference in mass between the nonframework iron-oxide particles and the silicate framework, iron

oxide particles as small as 2.5 nm could be observed in the transmission microscope images. In samples of Fe-ZSM-5 which had been steamed for 4 hours at 700°C two ranges of particles were observed. Very large 14-16 nm particles were found at the edges of the crystals at high iron content ($\text{SiO}_2/\text{Fe}_2\text{O}_3 = 54$) while 4 -7 nm iron clusters appeared to be trapped within the pores regardless of iron content. Smaller clusters of iron were observed to form (11 nm) when the iron was in more dilute concentration in the material. In an unstirred sample prepared under the same conditions, a larger variability in particle size was observed. These results are shown in Table 4 below.

Under milder steaming conditions (550°C for 1, 2 or 4 hours) only very small (2.5-4 nm) size particles inside the crystallites could be observed. Longer steaming times (12 hrs) identified a migration and small degree of agglomeration of the iron particles to the edge of the crystals. The size of the particles, after prolonged steaming still did not approach that observed at the higher temperatures indicating the effectiveness of the mild temperatures in maintaining secondary phase iron particle size.

Table 4: Iron oxide particle size imaged in the transmission electron microscope.

FeZSM-5(s, 4hrs, 700°C)			
SiO ₂ /Fe ₂ O ₃	size of Fe particles		
54	14-16 nm (edge)	4-7 nm (inside)	
92	11 nm	7 nm (inside)	4-7 nm few
175	11 nm	7 nm (inside)	none observed
FeZSM-5(s, 4hrs, 700°C)			
SiO ₂ /Fe ₂ O ₃			
200	4-7 nm (inside)	6-11 nm (outside)	
* Note: Non-uniform distribution			
FeZSM-5(s, 1, 2&4hrs, 550°C)			
SiO ₂ /Fe ₂ O ₃			
54	2.5-4 nm (inside)		
FeZSM-5(s, 12hrs, 550°C)			
SiO ₂ /Fe ₂ O ₃			
54	4-5.5 nm (edge)	2.5-4 nm (inside)	

SUMMARY OF THE RESULTS OF THE MODIFICATION PROCEDURE

- o Hydrothermal synthesis of TPA Fe(50), (90) and (200)
Highly dispersed iron in lattice framework sites.
- o Thermal treatment (550°C) to remove TPA
Some framework iron lost
- o Mild(550°C) hydrothermal treatment for 1 hr in 100% steam
Significant framework iron loss
- o Severe(550°C) hydrothermal treatment for 4 hrs in 100% steam
Further framework iron loss
- o 12 hr(550°C) hydrothermal treatment in 100% steam
Large iron oxide particle agglomeration
- o High temperature (700°C) hydrothermal treatment for 4 hrs in
100% steam - Large particle agglomeration of iron oxide

SYN-GAS ACTIVITY

A preliminary examination of the ability of two of the catalysts [Fe(90) calcined and steamed 1 hr at 550°C] was undertaken. Silicalite was used as a reference catalyst as it is expected to exhibit no activity in this reaction and was, therefore, used as a diluent for the modified ferrisilicate catalysts. No C₂+ hydrocarbons are formed over the silicalite catalyst. Overall the activity of the steamed ferrisilicate catalyst for the production of C₂+ products was higher than that of the thermally treated catalyst. Such results are expected as the amount of active non-framework iron is greater for the hydrothermally modified material determined by the physical characterization of these materials. The most notable difference between the two catalysts is the ability to produce olefinic products. The steamed catalysts sample shows a greater tendency to produce unsaturated C₂+ products beginning at 300°C than does the thermally treated catalyst.

CONCLUSIONS

Based on the results obtained in these studies, three factors contribute to the product distribution observed using the modified ferrisilicate catalysts: 1) high dispersion, 2) agglomeration, and 3) intrinsic framework acidity. The calcined ferrisilicate (high dispersion, low agglomeration) produces almost exclusively alkane products and products with carbon numbers greater than 5 which may be attributed to the presence of acidity, albeit weak, contribution from the ferrisilicate framework. Mild hydrothermal modification of this material (moderate dispersion, moderate agglomeration, very low acidity) produces both alkane and alkene products with sensitivity with temperature observed for the C₂ alkenes but not the corresponding alkane. The modification of ferrisilicate molecular sieves thus provides a level of control over product specificity in the reaction between CO and H₂. Examination of these catalysts under conditions which will produce higher carbon number products is presently under investigation.

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