

## CHARACTERIZATION OF $Fe_{1-x}S$ CATALYSTS SYNTHESIZED FROM FERRIHYDRITES UNDER DCL CONDITION

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### INTRODUCTION

Recently, considerable effort has been made to develop low cost, highly dispersed iron-based catalysts for direct coal liquefaction (DCL) [1]. Most iron-based catalysts are in fact the catalyst precursors as the catalysts convert to  $Fe_{1-x}S$  (pyrrhotite) under DCL reaction conditions. There has been less work reported on the pyrrhotite phase, in terms of its morphology and structure, and how they influence DCL activity.

In the past, we have extensively investigated the structure and DCL activity of ferrihydrite (FHYD), a highly dispersed iron oxide with surface area  $>200 \text{ m}^2/\text{g}$  and average particle size of 30-50 Å. The major drawback of this material as a catalyst is that the small particles quickly agglomerate and transform to a low surface area hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) at  $T > 200^\circ\text{C}$ . Moreover, the presence of surface adsorbed water molecules accelerates the agglomeration and phase transformation [2, 3]. This problem has been resolved by chemisorption of small amounts of impurity anions at the surface of ferrihydrite. The impurity anions block the crystal growth sites and thereby effectively inhibit the phase transformation to hematite, allowing the catalyst to maintain its dispersion. A number of binary ferrihydrite catalysts (M/FHYD, M/Fe  $\approx 5\%$ ) with M = Si, Mo, P, and citric acid (CA) have been synthesized in our laboratory [4, 5]. DCL tests using Si/FHYD and CA/FHYD show significant increases of coal-liquid conversion over that obtained from thermal reaction, or with pure ferrihydrite [4, 5].

In this paper, we report the characterization of pyrrhotite catalysts synthesized under simulated DCL conditions using binary ferrihydrites as the catalyst precursors. TEM, XRD, and Mössbauer spectroscopy were used for the characterization.

### EXPERIMENTAL

Three ferrihydrites were used: a pure ferrihydrite catalyst (30-Å catalyst) provided by Mach I, Inc., and two binary ferrihydrites Si/FHYD and CA/FHYD synthesized in our laboratory. Details of the synthesis can be found in Ref. 4 and 5.

Sulfidation of the catalysts was performed in a tubing bomb under simulated DCL conditions. The tubing bomb was loaded with 0.25 g of catalyst mixed with tetralin along with dimethyl disulfide (DMDS) as a sulfur donor (S/Fe = 2/1, by weight). The tubing bomb was than pressurized with  $H_2$  to 1000 psi at room temperature and agitated vertically at 400 cycles/min in a fluidized sand bath at  $415^\circ\text{C}$  for one hour. After reaction, the samples were subjected to XRD, TEM and Mössbauer investigation.

Mössbauer spectra were recorded using a constant acceleration spectrometer. The radioactive source consists of  $\sim 50 \text{ mCi}$  of  $^{57}\text{Co}$  in a Pd matrix. Powder X-ray diffraction (XRD) was performed on an automated Rigaku Dmax X-ray diffractometer. Transmission electron micrographs (TEM) were obtained with a Hitachi H800 NA scanning transmission electron microscope (STEM).

### RESULTS AND DISCUSSION

**TEM** For the pure ferrihydrite (30-Å), after sulfidation, TEM shows the formation of well crystallized, hexagonal-shaped  $Fe_{1-x}S$  particles with average particle size  $> 1000 \text{ Å}$  (Fig. 1). Similar result has been reported previously by Srinivasan et al [6]. Improved dispersion of the  $Fe_{1-x}S$  phase is obtained with the binary ferrihydrites as indicated in Fig 1, showing significantly smaller particles of less regular shape.

**X-ray diffraction**  $Fe_{1-x}S$  has the NiAs structure in which each Fe is surrounded by six sulfur atoms, and Fe has 1, 2, or 4 vacancies among its 12 nearest Fe neighbors. The monoclinic ( $Fe_7S_8$ ) and hexagonal ( $Fe_9S_{10}$ ) phases are the most common ones. The phase transition of monoclinic to hexagonal occurs at  $\sim 300^\circ\text{C}$ . The XRD patterns for the three ferrihydrite catalysts after sulfidation are consistent with those for the hexagonal phase (Fig. 2). However, the

pyrrhotite phase formed with Si/FHYD shows diffraction features on the high 2θ sides of the major diffraction peaks, which are also seen in the monoclinic phase (Figure 2a, indicated by arrows). Because of decreased Fe:S ratio, the d spacing for the monoclinic phase is shorter than that for the hexagonal phase, thus the (102) peak for the monoclinic phase is shifted to higher 2θ. Such shifting is also found for the sulfided Si/FHYD and the 350°C sulfided 30-Å catalyst, indicating incomplete mono-hex transition, due to the presence of the surface adsorbed Si and lower sulfiding temperature, respectively. For reasons unclear at the present time, the (102) peak for the sulfided CA/FHYD is shifted to the low 2θ side.

**Mössbauer spectra** Quantitative analysis for the Fe vacancies in pyrrhotite are obtained using Mössbauer spectroscopy. The Mössbauer spectrum for the hexagonal phase contains three sextets with magnetic hyperfine fields of  $H_i = 302, 274,$  and  $256$  kOe, respectively [7]. These three components are assigned to three Fe positions, which respectively have 0 (position A), 1(B), and 2(C) vacancies among their Fe neighbors. For the monoclinic pyrrhotite, the spectrum also consists of three sextets of  $H_i = 300, 256,$  and  $225$  kOe, corresponding to the Fe atoms with 0 (A), 2(C), and 4(D) vacancies in their Fe neighbors. Figure 3 shows the Mössbauer spectra of the three pyrrhotite catalysts. The spectrum for the sulfided 30-Å catalysts is very similar to that for hexagonal phase, which is dominated by the A, B, and C positions. However, a fourth component (D) is discernable, hence the spectrum is fitted with four sextets. The spectrum for the sulfided Si/FHYD is similar to that for the monoclinic phase, showing splitting of the absorption lines, due to decreased population of the B position and increased population of the C and D positions. The spectrum is fitted with three sextets representing the A, C, and D positions, and a doublet at the center for the unsulfided ferrihydrite. The results are in agreement with the XRD results. The spectrum for the sulfided CA/FHYD also shows increased splitting of the absorption lines as compared with that for Si/FHYD, indicating increased fractions of the C and D components. The spectrum is fitted with four sextets. The Mössbauer parameters are listed in Table 1.

According to the distribution of the four magnetic components (Table 1), a measure of the vacancy content in the nearest Fe shell, V is given by

$$V = \frac{(m*1 + l*2 + k*4)}{(n + m + l + k)} \quad (1)$$

where n, m, l, k represent the normalized fractions of four positions with 0, 1, 2, 4 vacancies, respectively. V values for the three samples are listed in Table 1. Significant increase of the Fe vacancies are found in the sulfided Si/FHYD and CA/FHYD.

In conclusion, we found that in addition to improving the dispersion of the pyrrhotite phases, the presence of impurity anions at the ferrihydrite surface retards the mono-hex phase transition, thus more Fe vacancies are retained in the pyrrhotite phase. The role of these Fe vacancies on catalytic coal liquefaction will be further investigated.

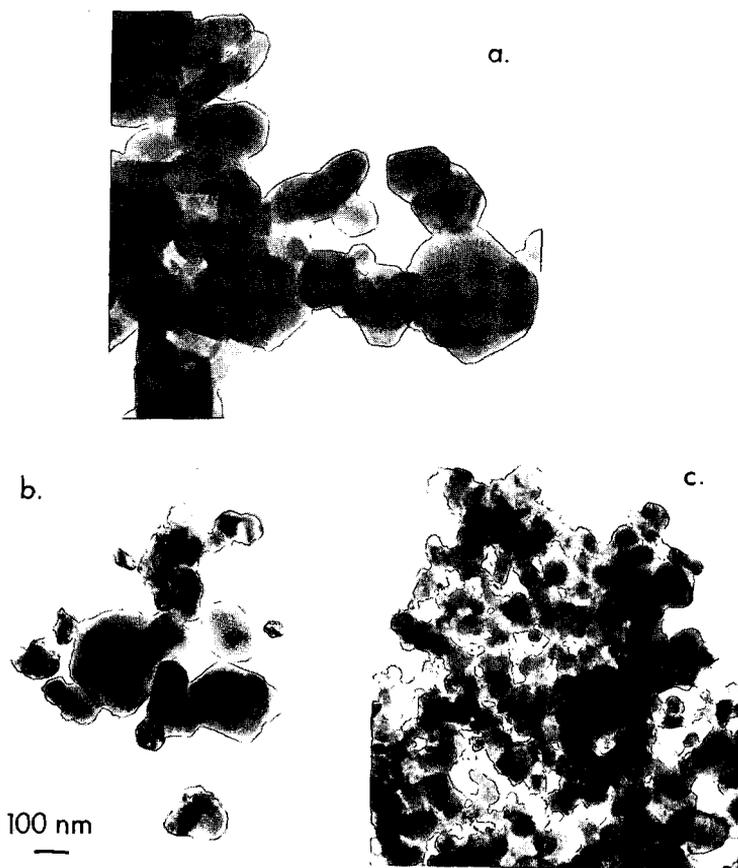
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**Table 1.** Mössbauer parameters for the ferrihydrite catalysts after sulfidation without coal. H is for the magnetic hyperfine field; IS the isomer shift; QS the quadruple splitting. A, B, C, and D represent the Fe positions with 0, 1, 2, and 4 Fe vacancies among its Fe neighbors. The average vacancy is determined by Eqn. (1). All spectra were recorded at room temperature.

Sample	H (kOe)	IS (mm/s)	QS (mm/s)	Phase	% Fe	V
30-Å	297	0.69	0.06	A	30.9	1.22
	274	0.72	0.04	B	31.2	
	257	0.69	0.07	C	30.5	
	232	0.60	0.11	D	7.4	
CA/FHYD	296	0.69	0.05	A	32.3	1.35
	273	0.71	0.04	B	23.9	
	255	0.68	0.05	C	32.1	
	227	0.63	0.09	D	11.8	
Si/FHYD	294	0.68	0.05	A	30.0	1.59
	255	0.67	0.05	C	26.6	
	223	0.65	0.09	D	15.3	
		0.45	0.52	FHYD	28.0	



**Figure 1** TEM for three sulfidated ferrihydrites: a) the 30-Å catalyst; b) CA/FHYD; c) Si/FHYD.

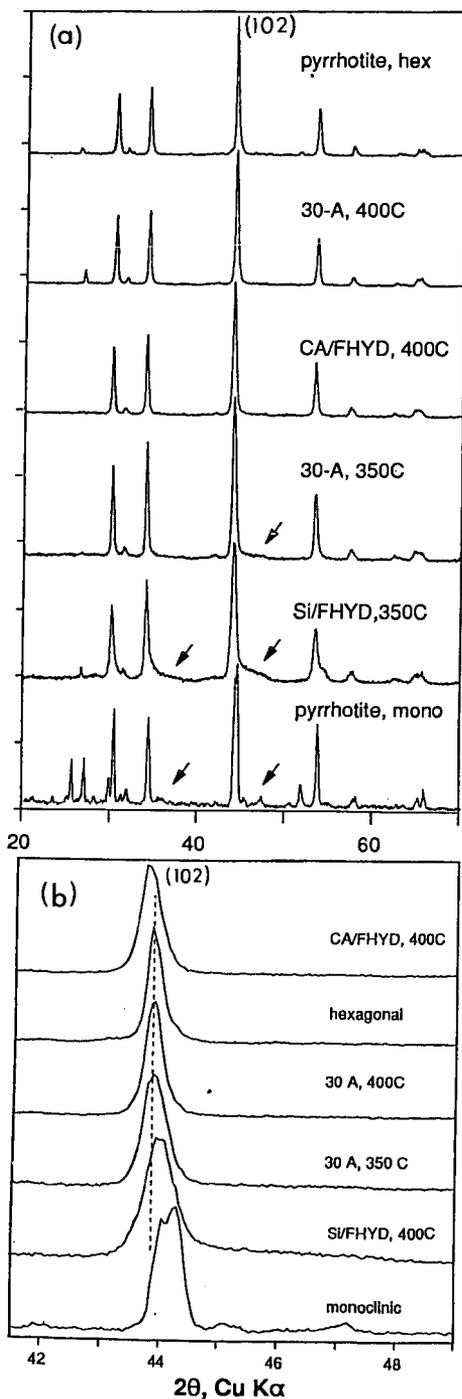


Figure 2. a) XRD patterns for the pyrrhotites and the sulfided ferrihydrate catalysts; b) the (102) peaks for the pyrrhotites and the sulfided ferrihydrate catalysts.

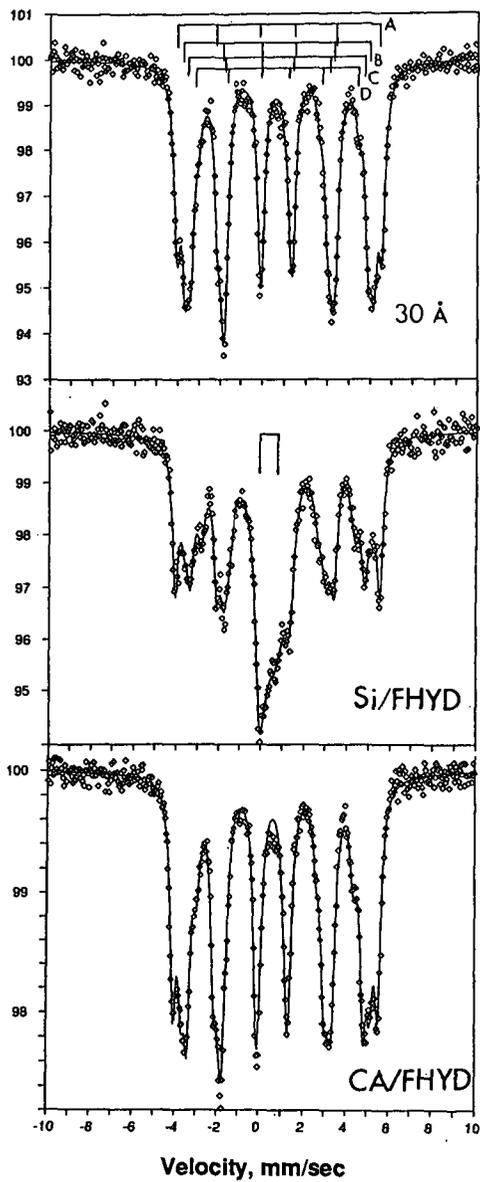


Figure 3. Mossbauer spectra of three sulfided ferrihydrites.