

CHARACTERIZATION OF IRON AND SULFIDED IRON OXIDE CATALYSTS BY ELECTRON MICRODIFFRACTION

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INTRODUCTION

The use of iron oxide as a catalyst for direct coal liquefaction was introduced soon after the initial discovery of the process (1-4). Iron oxide in the form of "red mud" has continued to be utilized (5). This was the catalyst of choice for the first stage reactor for many of the recent runs at the Wilsonville, Alabama Advanced Coal Liquefaction facility (6).

The availability of an ultrafine iron oxide catalyst (300 m²/g) provided an opportunity to follow with time the sulfidation of iron under mild direct coal liquefaction conditions. The use of transmission electron microscopy permitted a determination of the crystal structure and the elemental composition of individual catalyst particles.

EXPERIMENTAL METHODS

The Fe₂O₃ as-received powder was sulfided using dimethyldisulfide (DMDS) at 385°C for different periods ranging from 15 to 60 minutes.

For X-ray diffraction analysis, a Philips X-ray diffractometer equipped with an XRG-3100 generator, was used. The radiation used was CuK α ($\lambda_{\text{CuK}\alpha} = 1.548 \text{ \AA}$). A graphite monochromator was placed on the diffracted beam path. The data was acquired from the VAX/VMS V5.3-1 system.

Electron microscopy work was done using a Hitachi H800 NA scanning transmission electron microscope (STEM) at an operating voltage of 200 kV. This STEM is equipped with a silicon-lithium diode detector (Link) and a multichannel analyzer (Tracor 500). The X-rays emitted by the specimen upon electron irradiation were collected in the range 0-20 KeV for 60 seconds.

RESULTS AND DISCUSSION

The Fe-S system is so complex that various phases could be obtained as a result of sulfidation process. Numerous crystalline phases that exist in this system are presented in Table 1.

The precursor used for sulfidation studies was Fe₂O₃ (Mach Inc.). The surface area of these powders was 300 m²/g. The electron micrograph obtained from this as-received material is presented in Figure 1. An electron microdiffraction pattern obtained from a 5 nm region is shown in the inset in Figure 1, indicating that the material may be amorphous.

A particle size analysis indicates that the major fraction of the particles lies in the range 1-3 nm in diameter.

A typical X-ray diffraction pattern for the catalyst Fe_2O_3 -sulfided for 15 minutes at 385°C is shown in Figure 2. The X-ray peak intensities and the Bragg positions of 2θ correspond clearly to Fe_7S_8 phase. This is a hcp system with $a_0 = 0.686$ nm and $c_0 = 1.7062$ nm. All the $\{hkl\}$ indices corresponding to each profile are shown in this figure. The X-ray diffraction patterns obtained from other samples sulfided at longer times exhibited clearly the Fe_7S_8 (hcp) phase similar to that shown in Figure 2. However, the intensity was found to increase proportionately with the period of sulfidation time at 385°C . Thus, the crystal phase developed in all the catalysts is Fe_7S_8 according to the X-ray diffraction data (compare Table 1).

An electron micrograph obtained from the sample Fe_2O_3 sulfided at 385°C for 15 minutes is presented in Figure 3. Larger hexagonal crystals are formed after sulfidation at 385°C for 15 minutes. Several electron microdiffraction patterns were obtained from numerous individual crystals.

EDX analysis was also carried out along with the microdiffraction study. The particles appear to have grown into large hexagonal crystals, and yielded strong X-ray signals for $\text{Fe}_{K\alpha}$ and $\text{S}_{K\alpha}$ lines. Similar results were obtained for the Fe_2O_3 catalyst sulfided for 30 minutes. Likewise, large dense hexagonal crystals were observed for the one sulfided for 60 minutes. Similar size particles were obtained for either 15 minute and 60 minute sulfidation. Once the small oxide particles have undergone sulfidation for 15 minutes or more, they have grown to form hexagonal crystals which are larger than the precursor oxide particles, which show various iron sulfide phases. However, the majority of the diffraction patterns correspond to the Fe_7S_8 phase.

Ferric naphthanate was sulfided at 385°C for 15, 30 and 60 minutes respectively, under the same experimental conditions described above. A typical electron micrograph obtained from the 60 minute sulfided sample is shown in Figure 4(a) and a single hexagonal crystal is presented in Figure 4(b). The particle morphology for this catalyst is different from the other samples described above. The particles, although hexagonal in shape, consist of imperfections such as holes and dislocations. One such dislocation emanating from the boundary of the crystal can be seen in Figure 4(b). Several electron microdiffraction patterns revealed the structure to be FeS_2 , FeS and Fe_7S_8 .

The primary question plaguing the scientific community working in the area of direct coal liquefaction is the state of iron. Whether the iron oxide undergoes a phase transition directly to Fe_xS_y phases or it transforms to metallic iron first and then goes to form Fe_xS_y is the question to be addressed. While the major crystalline phase after sulfidation at 385°C for 15 minutes or more remains Fe_7S_8 , evidence was presented to show the existence of minor amounts of other Fe_xS_y phases. No evidence was found for the existence of metallic iron in the sulfided iron catalysts nor in the sulfided ferric naphthanate catalysts. It therefore appears that 15 minutes of sulfidation produces large iron sulfide crystals.

ACKNOWLEDGMENT

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Table 1

Crystalline Phases in Fe-S System

Formula	Crystal Structure	Lattice Parameters Å		
		a	b	c
Fe ₇ S ₈	HCP	a = 6.867	c = 17.062	
FeS	HCP	a = 5.967	c = 11.735	
Fe ₃ S ₄	HCP	a = 3.47	c = 34.5	
Fe _{1-x} S	HCP	a = 6.88	c = 22.90	
FeS ₂	Cubic	a = 5.417		
FeS	Cubic	a = 5.423		
Fe ₇ S ₈	Monoclinic	a = 11.902	b = 6.859	c = 22.787
β-Fe _{1-x} S	HCP	a = 6.894	c = 40.15	
Fe ₉ S ₈	Tetragonal	a = 3.679	c = 5.047	
FeS ₂	Orthorhombic	a = 4.436	b = 5.414	c = 3.381
Fe ₃ S ₄	Cubic	a = 9.876		
FeS	Tetragonal	a = 3.676	c = 5.032	

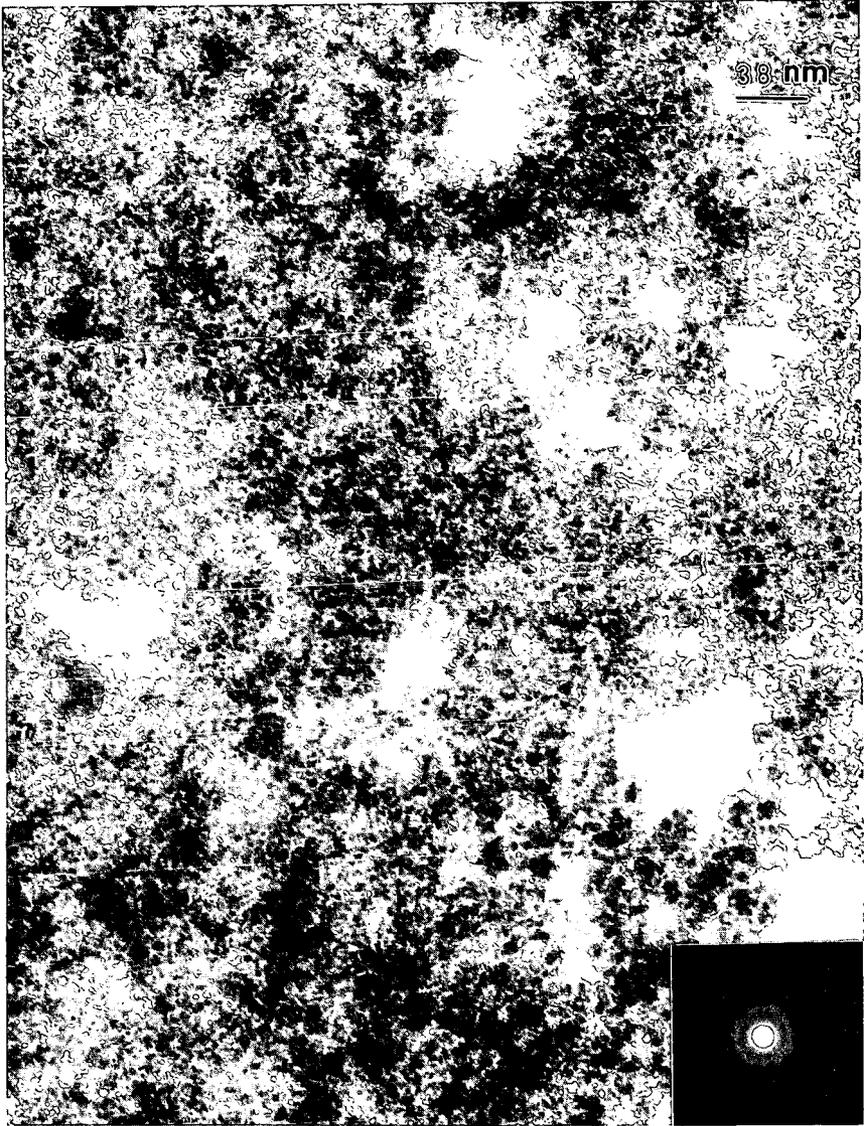


Figure 1. Transmission electron micrograph from the as-received Fe₂O₃ catalyst (inset). Microdiffraction pattern showing diffuse rings.

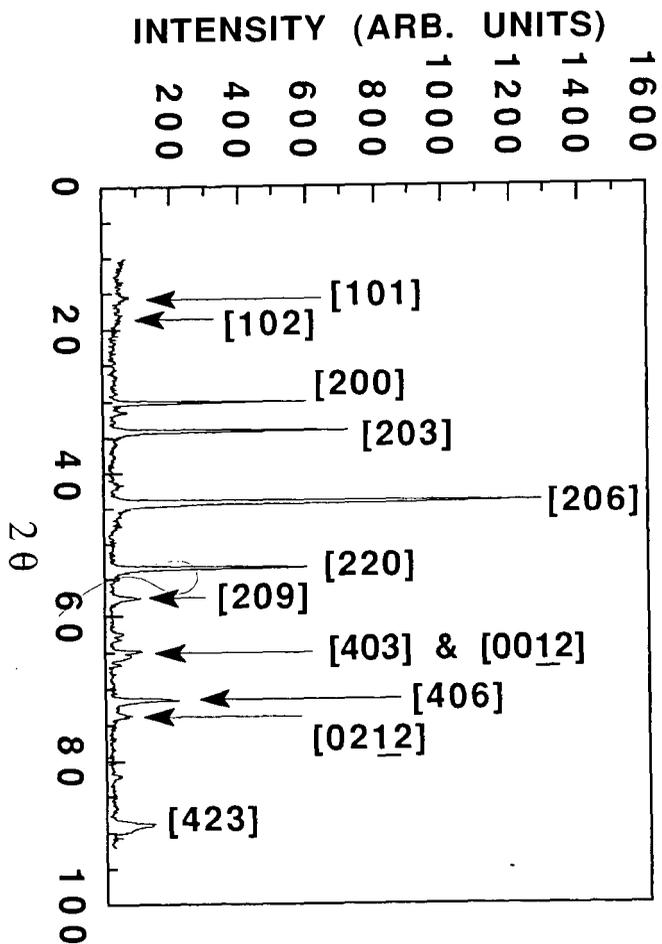


Figure 2. X-ray diffraction pattern from the Fe_7S_8 catalyst sulfided at 385°C for 15 minutes showing the Fe_7S_8 (hcp) phase.



Figure 3. Transmission electron micrograph from the as-received Fe₂O₃ catalyst after sulfiding at 385°C for 15 minutes showing large hexagonal crystals.

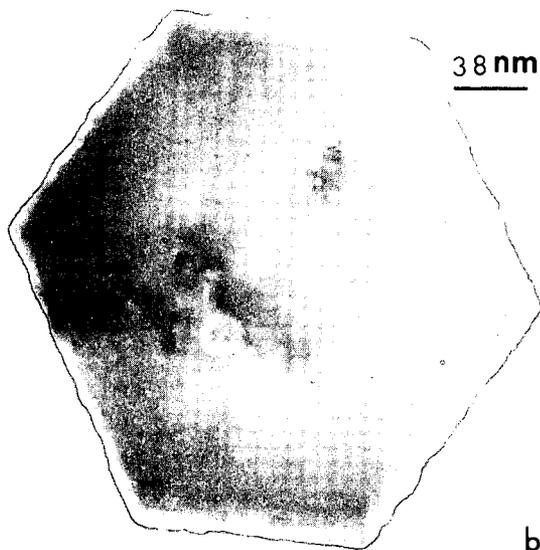
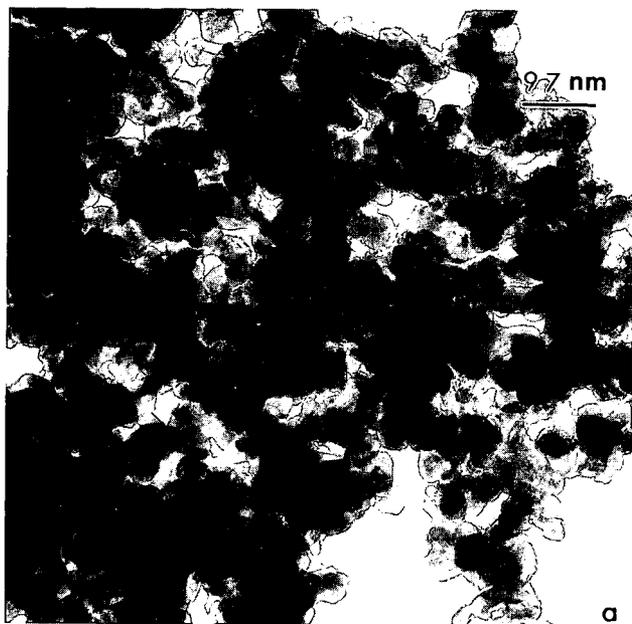


Figure 4. (a) A naphthalene electron micrograph obtained from ferric naphthanate after sulfidation at 385°C for 60 minutes. (b) A large single hexagonal crystal from the above sample.1