

Iron Sulfide Catalysis in Coal Liquefaction

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I. Introduction

The direct liquefaction of coal is a process that involves the interaction between coal, hydrogen, solvent, and catalysts. Mineral matter has been known to enhance the conversion of coal to liquid products.^(1,2,3) Addition of pyrite, pyrrhotite, and liquefaction residues to coal has been shown to affect the coal conversion yields and the viscosity of the products.⁽⁴⁾ Of all the minerals present in coal, pyrite (and marcasite) are the most important for coal utilization, especially in direct coal liquefaction.^(1,5) However, one has to remember that under coal liquefaction conditions pyrite rapidly transforms to a non stoichiometric iron sulfide $Fe_{1-x}S$ ($0 < x < 0.125$). It is noted that the sulfur formed as a result of the decomposition of pyrite is able to extract hydrogen from poor donor solvents. The stoichiometry of the pyrrhotite formed from FeS_2 depends strongly on the partial pressure of H_2S .⁽⁶⁾

A correlation between the conversion of coal to benzene soluble, and the stoichiometry of the iron sulfides was observed by Montano and Granoff.⁽⁷⁾ Higher conversion is accomplished by a more iron-deficient pyrrhotite.⁽⁸⁾ Stephens et al studied the effect of additives to an IL#6 conversion to liquid products. Their work strongly suggests that $Fe_{1-x}S$ and H_2S play a catalytic role in the conversion of coal to oils. These results, in good agreement with the ones obtained from in situ Mössbauer measurements,^(9,10) where there was clear evidence of interaction between the iron sulfides and some coal components. Many questions remain unanswered concerning the catalytic roles of H_2S and $Fe_{1-x}S$. Lambert⁽¹¹⁾ suggested that the catalytic activity observed for pyrite is solely due to H_2S acting as a hydrogen-transfer catalyst. In a recent study by Anderson and Bockrath on direct coal liquefaction more conversion was obtained when the ratio of sulfur added to an iron solution (the catalyst) was equal to the one needed to obtain pyrrhotite ($Fe_{1-x}S$). A very recent work by Ogawa, Stenberg, and Montano⁽¹²⁾ reporting the hydrogenation of diphenylmethane in the presence of pyrrhotite clearly shows that maximum activity is obtained when the partial pressure of H_2S is enough to maintain an iron deficient surface. Too high a partial pressure of H_2S in the reactor moves the composition of the surface towards FeS_2 and the conversion of diphenylmethane is reduced. Too low a partial pressure of H_2S leads to the formation of troilite (FeS) and lower conversion. These results indicate that optimum conditions are obtained when the surface of the sulfide is rich in metal vacancies, where dissociation of H_2S can take place forming highly reactive species.⁽¹³⁾ It is obvious that the understanding of the catalytic role of the iron sulfides lies in the investigation of their surface properties. We report in the present paper such a study, where surface techniques were used to observe the reaction of gases found under liquefaction conditions with the sulfides surfaces. A special reactor was developed to study the surface composition of the iron sulfides after reaction with oxygen containing compounds using conversion electron Mössbauer spectroscopy (CEMS). Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) were used for determining the environment of iron species in the residues obtained from the study of the interaction of iron sulfides (FeS_2, Fe_7S_8) with pyrene.⁽¹⁴⁾

II. Experimental

Auger and electron energy loss spectroscopy measurements were performed using an UHV system with a base pressure of 10^{-10} torr. The system was attached to a reactor cell where the samples were exposed to high temperatures and gases. The reactions of FeS_2 , Fe_7S_8 , and FeS with CO , H_2 , O_2 , NH_3 , CH_4 , C_2H_4 , and higher hydrocarbons were studied between room temperature and 450°C . Figure 1 shows a schematic diagram of the system used in these measurements.

The CEMS measurements were carried out in a specially designed reactor to be described elsewhere. In this reactor the samples of ^{57}Fe foil were studied and treated with $\text{H}_2/\text{H}_2\text{S}$ to obtain the iron sulfides. The detector employed for the detection of the electrons was a $\text{He}/10\% \text{CH}_4$ flow counter connected in line with the reactor. The reaction of pure iron and iron sulfide with naphthoquinone were studied with this cell. The EXAFS and XANES measurements of the residues of the reactions of FeS_2 and Fe_7S_8 with model compounds were made at the Cornell High Energy Synchrotron Source.

Experimental Results

1. Auger and Electron Energy Loss Measurements on FeS_2 , Fe_7S_8 , FeS

Natural crystals of FeS_2 (pyrite) and Fe_7S_8 (monoclinic pyrrhotite) were used for the measurements. The (100) face of pyrite and the (0001) face of pyrrhotite were studied in the reactor, using a polycrystalline sample of FeS . All the samples show a characteristic $M_{2,3}$ VV Auger doublet with a separation of 5.0 eV (Figure 2). Two additional peaks (3 and 4 in Figure 2) are also observed for FeS . Peak 1 may correspond to transitions involving the s-3p ($2\sigma_v$) valence band while peak 2 may correspond to transitions involving the d-band. A typical set of Electron Loss spectra for FeS_2 is shown in Figure 3. Peak a is assigned to interband transitions from the $\text{Fe-}3d$ band to an empty state above the Fermi level. Peaks b and c may be assigned to transitions for one s-3p-like valence band (peak b to $1\pi_g \rightarrow 2\sigma_v$ and c to $2\sigma_g, 1\pi_u \rightarrow 1\sigma_g$ transitions.) Peaks d and e are attributed to collective oscillations of the conduction or valence electrons. Peaks f and g are assigned to surface and volume plasmons respectively. Peaks j and k are transitions involving the Fe-3p electrons ($M_{2,3}$ level). Peak l is due to transition from the M_1 level. The EEL spectra for the other sulfides are similar but the position and intensities of the peaks vary. In our measurements we observed EEL peaks with strong iron or sulfur character. Damaged iron sulfide surfaces show evidence of reconstruction through migration of sulfur after heating to 450°C . For undamaged sulfides, heating results in changes in the chemical composition of the surface; migration of sulfur also occurs. There is clear evidence of the presence of elemental sulfur on the pyrite and pyrrhotite surface but not on troilite (FeS). Since the maximum temperature attained was 450°C we do not expect that reduction of the FeS surface will take place. Essentially if the partial pressure of H_2S is low in the reactor the formation of FeS will occur by removal of sulfur from the Fe_{1-x}S surface. Once this state is reached no further loss of sulfur occurs and a fairly stable surface is obtained.

The interaction of the pyrrhotite with simple gases is more complex, damaged surfaces of FeS_2 and Fe_7S_8 react with CO at 450°C . We understand that as the result of the interaction of CO with Fe on the sulfide surface. This interaction is not detected with undamaged surfaces (pure single crystals) and with FeS . The formation of oxides on the surface is easily detected for FeS_2 and Fe_7S_8 after reaction with CO . It has been observed that CO undergoes a disproportionation reaction on Fe, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, with the formation of surface oxide due to the

dissociation of CO. (16) The surface oxide is rapidly removed by H₂. The surfaces of the sulfides do not show any evidence in the Auger and EEL spectra of reactions with NH₃, CH₄, and C₂H₄. However, they interact strongly with molecular oxygen forming a surface oxide. Figure 4 shows the surface oxide formed on pyrite after interaction with oxygen, for comparison purposes the EEL spectrum for α -Fe₂O₃ is also shown. The present measurements indicate a high reactivity of the sulfide surfaces towards oxygen containing compound and very little towards light hydrocarbons and ammonia.

2. CEMS Measurements of the Surface Interaction of Naphthoquinone with Iron and Iron Sulfide Surfaces

A high purity ⁵⁷Fe foil was used for these measurements, such a foil was necessary in order to record rapidly a Mössbauer spectrum (less than one-half hour). The sample was placed in the holder inside of the reactor and H₂ was flown for 2 hours at 350 °C to reduce the surface and clean off any residual contamination. Figure 5a shows the Mössbauer spectrum at room temperature inside the reactor after cleaning. We studied the hydrogenation of naphthoquinone by introducing about 20 mg of the compound and flowing hydrogen at about 0.5 cc/sec. The temperature of the reaction was 305 °C and 405 °C and the time of reaction was one-half hour. After reaction the CEM spectrum was taken inside the reactor. No evidence of the formation of any known oxide was detected (Figure 5b). The same experiment was repeated using a sulfided sample (produced from the ⁵⁷Fe foil by flowing H₂/H₂S (10%) at 400 °C). The spectrum for such a sample is shown in Figure 6a before reaction. After reaction with naphthoquinone we see clear evidence of the formation of Fe₃O₄ on the surface (Figure 6b). Magnetite is formed at the expense of the iron sulfide. This observation is in very good agreement with our earlier *in situ* Mossbauer work, (14) where a less surface sensitive technique was used for the measurements. We interpret these results as evidence of a greater reactivity of the iron sulfides surfaces towards oxygen containing organic molecules than the pure metal. It is noted that magnetite can be easily removed by further flow of H₂/H₂S. The magnetite layer is formed in the first few surface layers of the iron sulfide (see Figure 6).

3. EXAFS and XANES Measurements

Measurements were performed on the residues of the reaction of FeS₂ and Fe₇S₈ with pyrene. Pyrite and monoclinic pyrrhotite were used as chemical standards for the measurements. In Figure 7 the XANES spectra are shown for the residues of the reactions of pyrene with Fe₇S₈ and FeS₂. The reactions were performed (14) at 440 °C in the presence of H₂. One notices that the near edge structure is different for both residues, we attributed the difference to the presence of FeS in the reaction residues of Fe₇S₈ and pyrene. A compound that is not present in the residues of the pyrite run. The total EXAFS spectrum were analyzed and the Fourier transform for the residues of the FeS₂ run is shown in Figure 8a. (The peak positions are not corrected for phase shifts.) For comparison purposes the Fourier transform for pure pyrite and monoclinic pyrrhotite are also shown. The first prominent peak in all the spectra is due to Fe-S distances (2.262 Å for pure FeS₂). The second peak in pyrite (Figure 8b) is due to the other iron neighbors. For Fe₇S₈ the spectrum is complicated since there are many iron distances present (Figure 8c). For the residues of the reaction of FeS₂ with pyrene practically no Fe-Fe can be identified. This means that the iron atoms and vacancies in the Fe_{1-x}S structure (14) (atomic % iron is 47.8) are extremely disordered and randomly distributed and that the only well defined coordination of the iron ions are the sulfur atoms. This (14) striking result since we should have expected as a result of the Mössbauer study (14) a better defined pyrrhotite structure.

III. Conclusions

We have observed that the behavior of iron sulfide surfaces depends strongly on the stoichiometry. Iron deficient surfaces show a higher reactivity than the troilite surface. At high temperatures (450 °C) there is elemental sulfur present on the iron sulfide surfaces. The metal vacancies can serve as centers for the dissociation of H₂S thus facilitating the transfer of hydrogen to organic entities. The pyrrhotite surface shows a great reactivity towards oxygen containing compounds. The surface oxide formed on the pyrrhotite surface are easily reduced when H₂ and H₂S are present in the reactor. The interaction between the pyrrhotites surfaces and light hydrocarbons is minimal.

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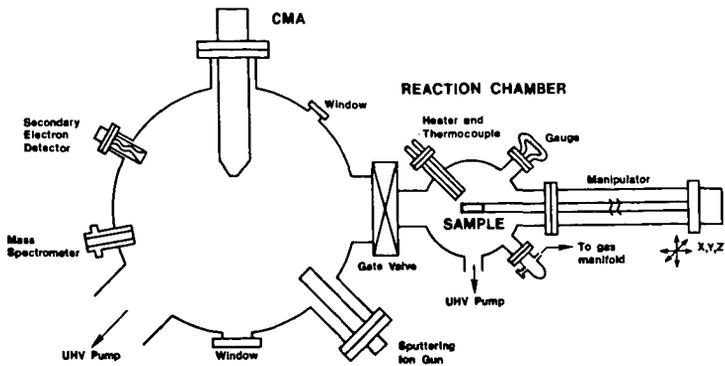


Figure 1. Schematic diagram of the UHV system used for the surface measurements

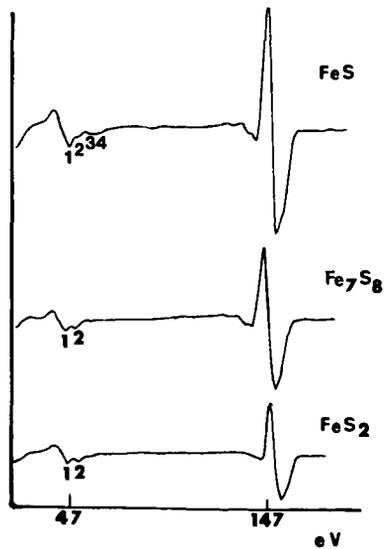


Figure 2. Low energy Auger spectra for the iron sulfides

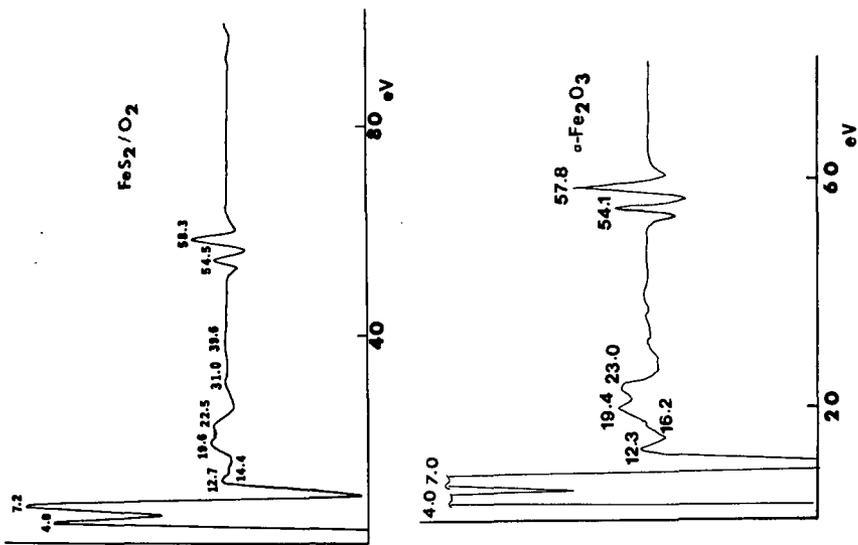


Figure 4. EEL spectra of FeS₂ after reaction with oxygen (a) and of α-Fe₂O₃ (b)

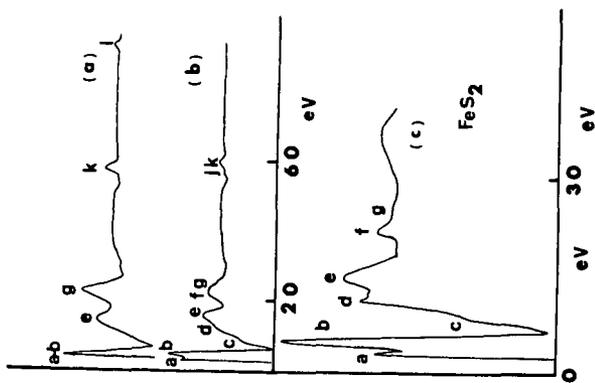


Figure 3. EEL spectra for FeS₂
 a) E_{primary} = 300 eV b) E_{primary} = 150 eV c) E_{primary} = 50 eV

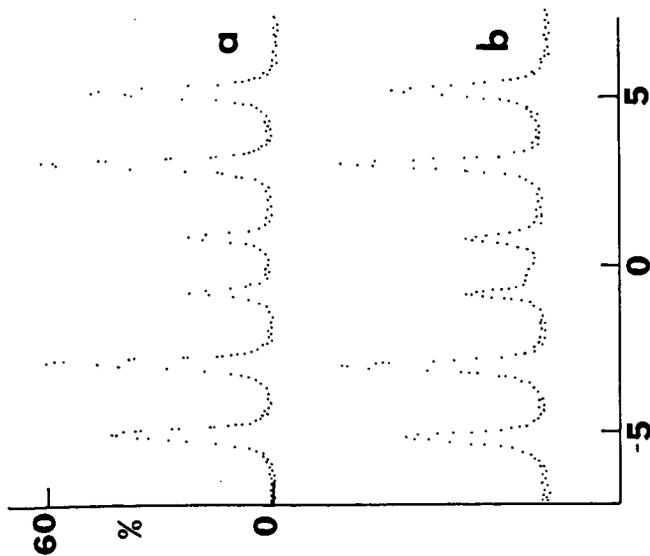


Figure 5. CEM spectra of ^{57}Fe foil (a) and after reaction with naphthoquinone (b). X-axis is in mm/sec.

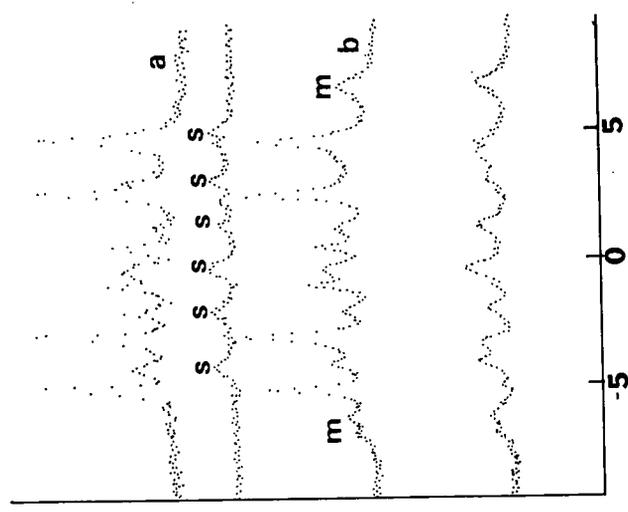
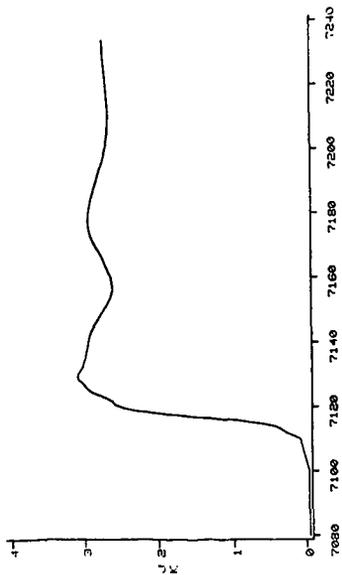


Figure 6. CEM spectra of a) sulfided ^{57}Fe foil, s; indicates the sulfide surface b) After reaction with naphthoquinone m; magnetic, bottom spectrum is the surface layers after reaction. X-axis is mm/sec.

FeS₂+H₂+PYRENE
AFTER BACKGROUND SUBSTRUCTION



Fe₇S₈+H₂+PYRENE
AFTER BACKGROUND SUBSTRUCTION

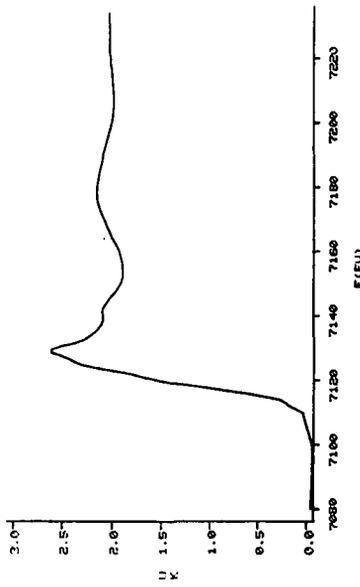


Figure 7. XANES spectra of the residues of the reactions of pyrene with a) FeS₂ and b) Fe₇S₈

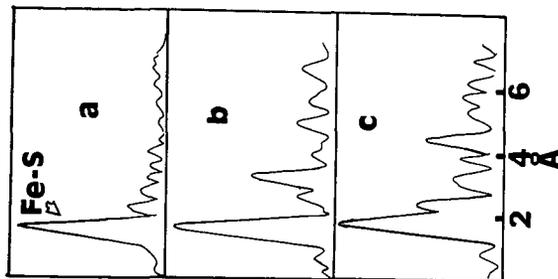


Figure 8. Fourier transforms of $\chi \cdot k$ (x EXAFS structure) for a) FeS₂ after reaction b) pure FeS₂ and c) Fe₇S₈. X-axis is in Å and without corrections for phase shifts.