In-Situ Study Under Direct Coal Liquefaction Conditions of the Surface Interaction Between Iron Sulfides and Selected Number of Model Compounds

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Abstract:

The importance of iron sulfides in direct coal liquefaction has been noted by several investigators; an increase in coal conversion and quality of the products has been observed in their studies. In order to gain a better understanding of the role of iron sulfides in coal liquefaction we have investigated "in-situ" the interaction of FeS_2 and Fe_7S_8 with a series of model compounds. In our experiments 10% catalysts by weight were added to the model compounds. The model compounds studied were dibenzothiophene, pyrene, phenanthrene, 1,4-naphthoquinone, phenothiazine, and quinoline. The experiments were performed in nitrogen and hydrogen atmospheres. We find evidence of interaction between the pyrrhotites and some of the model compounds. The formation of intermediate iron oxides in 1,4-naphthoquinone indicates a strong interaction between the iron on the pyrrhotite surface and oxygen. The surface composition of pyrrhotite at 450°C was also studied in a UHV reaction chamber and the interaction with H_2, O_2 and CO was investigated using electron energy loss spectroscopy.

I. INTRODUCTION

Direct coal liquefaction is a process that has been known for a number of years. The liquefaction of coal is a complex process involving a close interaction between coal, hydrogen-donor solvent, and catalysts. The role of mineral matter and particularly iron sulfides in coal liquefaction has been the subject of several investigations (1-3). Mukherjee and Chowdbury observed an increase in coal conversion in the presence of mineral matter (2). Recycling the mineral matter tends to increase the reaction rate and enhance the conversion of pyridine-solubles to benzene solubles (4). The addition or presence of pyrite enhances the production of liquid products from coal (5). The specific effect of each mineral has not been well established (6) because some of the minerals occur in very small amounts. Some of the clay minerals may have only a simple physical effect (6). All the experimental results suggest the iron sulfides as the most actively involved minerals in coal liquefaction.

It has been observed that the conversion to liquid products for four different coals correlates with the stoichiometry of the pyrrhotites present in the residues (7). Stephens et.al. (8) carried out a series of experiments with various additives on an ILL#6 coal and observed an enhancement in conversion to benzene solubles with the addition of pyrrhotite and H_2S. Mössbauer studies (9,10) of the iron sulfides in coal indicate the existence of an interaction between coal components and the pyrrhotites at high temperatures. These experiments suggest an active role of the pyrrhotites in coal liquefaction. However, still many questions remain unanswered concerning the catalytic roles of H_2S and $Fe_{1-x}S$. Lambert points out that the catalytic activity observed for pyrite is solely due to H_2S acting as a hydrogen transfer catalyst (11).

More research is needed in order to clearly distinguish between the role of H_2S and the behavior of the pyrrhotites during coal liquefaction. In a complex material such as coal, it is difficult to identify the roles of vastly differing organic functional groups and their interaction with $Fe_{1-x}S$ and/or H_2S. A simpler approach

is the study of model compounds. Several studies have appeared in the literature on the effect of pyrite and pyrrhotite on model compounds. Guin et.al.(12) studied the hydrogenolysis of benzothiophene in the presence of pyrite. The main product was 2,3-dihydrobenzothiophene. When pyrite was used, the selectivity was shifted toward ethylbenzene. Pyrite seems to catalyze the hydrogenation of pyrene to dihydropyrene (13). Bockrath and Schroeder (14) observed that when pyrrhotite is heated in tetralin, only dehydrogenation is catalyzed. We report in the present work "in-situ" Mossbauer measurements of FeS_2 and Fe_7S_8 in six different model compounds. The behavior of the sulfide surfaces is also studied using electron energy loss spectroscopy. In addition, the changes taking place on the surfaces during reactions with simple gases are investigated using this technique.

Experimental

The "in-situ" Mössbauer measurements were carried out using the reactor shown in Figure 1. A more detailed description of this reactor can be found in Reference (9). The FeS_2 and Fe_7S_8 additives used were from natural mineral samples and were characterized by x-ray diffraction and Mössbauer spectroscopy. In the experiments with model compounds, 10% catalyst (200 mesh) by weight was added and mixed with 1 gm of the model compounds. The model compounds studied using Mössbauer spectroscopy were pyrene, phenanthrene, dibenzothiophene, 1,4-naphthoquinone, phenothiazine and quinoline. The experiments were carried out at 440°C in a nitrogen or hydrogen atmosphere. The reaction time was one hour. The residues were measured at room temperature. The stoichiometry of the pyrrhotites present in the residues was determined using the method described in references (7,15). Data acquisition and analysis were conducted on a microprocessor-based computer. The source was a 200 mCi ^{57}Co:Rh. All the isomer shift values are given in reference to α-Fe at room temperature. The surface properties of FeS_2 and Fe_7S_8 we studied using Auger and electron energy loss spectroscopy. The samples were mounted in an UHV chamber with a specially-designed high pressure reactor. In this reactor the samples were exposed to various gases (CO, H_2, O_2) and high temperatures.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Mössbauer Measurements

The most important Mössbauer parameters in the study of the transformations and interactions of iron sulfides in coal are the isomer shift, the magnetic hyperfine and quadrupole splittings. The isomer shift (IS) results from the electrostatic interaction of the nuclear and electron charge distributions inside the nuclear region. The observed IS in the Mössbauer spectrum is the difference between the shifts in the source and absorber. The IS is given by the following relation:

$$IS = \frac{2\pi}{5} Ze^2R^2 \frac{\delta R}{R} \left(|\Psi_{abs}(0)|^2 - |\Psi_s(0)|^2 \right) \quad (1$$

The quantity $\delta R/R$ is a nuclear property and can be estimated using well characterized standards. The IS gives unique information on the valence state of the Mössbauer atom or ion. The range of IS values for iron compounds in reference to α-Fe covers values between -0.78 mm/sec for Fe^0 isolated in nitrogen to +1.9 mm/sec for Fe^+. (1 mm/sec = 0.48 x 10^{-7}eV for the 14.4 keV transition of ^{57}Fe.) The IS values reported include the second order Doppler shift (SODS). The SODS can

be easily distinguished by its temperature dependence. Its contribution to the present work is not large enough to justify the correction of the measured centroid.

The magnetic hyperfine splitting arises from the interaction of the nuclear dipole moment with a magnetic field due to the atom's own electrons. The Hamiltonian describing this interaction can be written as:

$$H_m = -\left(\frac{\mu}{I} M_I B\right) \qquad (2$$

where I is the spin of the nucleus, μ is the magnetic moment, M_I the magnetic quantum number, and B the magnetic field at the nucleus. For a pure magnetic interaction six transitions are possible between the 14.4 keV level (I=3/2) and the ground state (I=1/2). The presence of vacancies in the pyrrhotites results in a lower magnetic field at the iron ion; this feature is used to calculate the stoichiometry of the pyrrhotites in coal liquefaction residues. The atomic percentage of iron is calculated according to (15)

$$\text{at.\%Fe} = 100 \times \left[0.6836 \times 10^{-3} \times \bar{H}_{mhf} + 0.2881\right]$$

$$\bar{H}_{mhf} = \frac{1}{A_{Total}} \sum_i A_i H_i \qquad (3$$

$\bar{H}_{mhf}$ = average magnetic hyperfine field

A_{Total} = total Mössbauer spectral area

A_i = spectral area under i-th site

H_i = mhf on i-th site

The quadrupole splitting (QS) occurs when the Mössbauer ion electrons and/or the neighboring atoms produce an inhomogeneous electric field at the nucleus and when the nucleus possesses a quadrupole moment. The quadrupole splitting for the excited state 14.4 keV of ^{57}Fe is given by

$$QS = \frac{1}{2} e^2 qQ \left(1 + \frac{\eta^2}{3}\right)^{1/2}$$

where

$eq = V_{ZZ}$ = principal axis of the field gradient tensor

$$\eta = \frac{V_{XX} - V_{YY}}{V_{ZZ}} = \text{asymmetry parameter}$$

Q = quadrupole moment of the nucleus

The combination of IS and QS is very useful in the identification of minerals in coal. The procedure followed is to measure these parameters for standard well characterized compounds and to compare with the values obtained for the coal minerals.

The above Mössbauer parameters will be used to study the transformations and inversions of several model compounds with FeS_2 and Fe_7S_8.

A. Interaction and Decomposition of FeS_2 in the Presence of Model Compounds

Pyrene: Pyrite partially decomposes in the presence of pyrene even in the absence of hydrogen. The observed IS at 440°C for the sample in a nitrogen atmosphere is close to zero. The spectrum shows a well-defined doublet with a quadrupole splitting (QS) close to the value observed for pure pyrite. The spectrum of the residue shows the presence of a pyrrhotite with a stoichiometry close to that observed for Fe_7S_8, about 46% of the original pyrite remains unreacted. The conversion of pyrite to pyrrhotite is larger than the one obtained in the absence of pyrene. In the presence of H_2 the transformation of pyrite to pyrrhotite is complete. At 440°C the Mössbauer spectrum shows only a broad singlet with an IS = 0.35 mm/sec, this value is smaller than the one obtained for the pure pyrrhotites in the absence of pyrene (Table I). This is given as evidence of an interaction between the pyrrhotite and the gases present in the reactor. It is possible that what we observed in this experiment is an intermediate state of the iron on the pyrrhotite, probably interacting with molecular hydrogen and pyrene. The hexagonal pyrrhotite obtained after the reaction is very similar to the one observed in residues from coal liquefaction. H_2S apparently does not play any other role but that of controlling the H_2/H_2S ratio in the reactor.

Phenanthrene: The results of the Mössbauer measurements in a nitrogen atmosphere are very similar to those obtained for pyrene. There is partial conversion to $Fe_{1-x}S$ and the presence of a doublet with parameters close to those of pyrite at 440°C (no real evidence of an interaction). By contrast in the presence of hydrogen, the IS at 440°C is the same of pure $Fe_{1-x}S$. The conversion of pyrite to pyrrhotite is complete (Table II). We must again emphasize that the conversion of pyrite in the presence of the model compound is faster than in the absence of phenanthrene. If there is hydrogenation (1) of the phenanthrene, it is possible that the pyrrhotite does not play any direct role, or that the intermediates decompose faster than 10^{-7} sec (the lifetime of the Mössbauer level).

Dibenzothiophene: In the presence of this compound and in a nitrogen atmosphere, pyrite fully decomposes to $Fe_{1-x}S$. The pyrrhotite formed from this reaction has a stoichiometry close to that of Fe_7S_8 (Table II). There is evidence of interaction with DBZ at 440°C, a doublet is observed with IS close to zero and QS = 0.63 mm/sec (Figure 2). These values are similar to those of pyrite, however there is no pyrite left in the residues (Figure 3). In a hydrogen atmosphere the Mössbauer spectrum at 440°C is very different from that observed in nitrogen. A single Mössbauer line with an IS = 0.36 mm/sec is observed. The residue of this run is an hexagonal pyrrhotite. The present results indicate a reaction with the pyrrhotite. It is very probable that hydrogenation is the major catalytic role of the pyrrhotites in this system.

Phenothiazine: There is partial decomposition of pyrite in a nitrogen atmosphere, however in this case there is less decomposition than for pyrene or phenanthrene. Decomposition takes place in the presence of hydrogen but it is incomplete. The IS and QS at 440°C are clearly due to the unreacted pyrite (Table II). These measurements do not indicate any kind of strong reaction for FeS_2 or $Fe_{1-x}S$ with the model compounds. If any reaction occurs, it is very weak compared to pyrene, phenanthrene or DBZ.

Quinoline: There is only partial decomposition of pyrite to pyrrhotite in nitrogen or hydrogen atmospheres. The stoichiometry of the pyrrhotite present in the residues is very close to Fe_7S_8. In order to obtain such a stoichiometry, a high partial pressure of H_2S must be present in the reactor. The Mössbauer spectrum at 440°C can be attributed to FeS_2 alone; there is a very small contribution from the pyrrhotite and no evidence of reaction. These results suggest no active role for the pyrrhotite in catalyzing the hydrogenation of quinoline to tetrahydroquinoline

(THQ), only H_2S remains as a possible catalyst. We will come back to this problem when discussing the interaction with Fe_7S_8.

1,4-Naphthoquinone: A very interesting result is obtained when the reaction takes place in a nitrogen atmosphere. It is observed that Fe_3O_4 is present in the residue. In order for this to happen the pyrrhotite formed from the partial decomposition of pyrite must react with the oxygen present in the model compound. In a hydrogen atmosphere the magnetite is absent from the final products and full conversion of pyrite to pyrrhotite occurs. The present results indicate a strong affinity of the pyrrhotite surface towards oxygen, and indicates that breaking of oxygen bonds in coal is a possible mechanism by which coal conversion is enhanced.

B. Interactions and Transformations of $Fe_{7-8}S$ in the Presence of Model Compounds. (All the experiments in a hydrogen atmosphere.)

Pyrene: A single Mössbauer line is observed at 440°C with an IS ≈ 0.35 mm/sec. The residue shows the presence of FeS (troilite) and $F_{1-x}S$ with 48.2 at% Fe (Table III). Figures 4 and 5 show the Mössbauer spectra for this run at 440°C and room temperature respectively. The presence of troilite requires a very low partial pressure of H_2S in the reactor. This is not totally unexpected since the amount of free sulfur available from Fe_7S_8 is very limited. There is evidence of a reaction with the pyrene, but the sulfides obtained in this case differ markedly from those obtained for FeS_2. This difference may be attributed to the excess of H_2S when pyrite is the precursor of pyrrhotite.

Phenanthrene: The Mössbauer measurements in this case give very similar results to the ones obtained for pyrene. There is a reaction at 440°C; there troilite is present in the residues. These results contrast with the ones obtained when pyrite is added to phenanthrene. There is a marked difference between the behavior of the nascent pyrrhotite and Fe_7S_8. The excess of sulfur atoms on the pyrite surface is probably responsible for such a difference.

DBZ: There is evidence of a reaction at high temperatures (IS = 0.30 ± 0.06 mm/sec). The residue contains troilite. Since DBZ has sulfur, there must be a reaction between H_2S and the compound in order to effectively reduce the partial pressure of H_2S and allow the formation of FeS. There is evidence of active involvement of H_2S in the reactions.

Quinoline: There is some evidence of a reaction at high temperature (440°C), the IS = 0.40 ± 0.07 mm/sec close to that of pure pyrrhotite, but still slightly more negative. The residue of this run does not show any FeS, the pyrrhotite obtained has 48.2 at.% iron. We attribute this behavior to the presence of unreacted H_2S, otherwise FeS can be formed. This behavior is different from that observed for pyrite, again pointing out the difference between the nascent pyrrhotite (from pyrite) and Fe_7S_8.

Phenothiazine: Similar results to those obtained for quinoline, but in this case the at.% iron in the residues is lower (Table III). This last result is clear evidence of a higher partial pressure of H_2S in the reactor. This behavior contrasts with the one observed for DBZ. In both molecules sulfur is present, however in phenothiazine there is also nitrogen. It is tempting to attribute some reactivity to the pyrrhotite and nitrogen, although the present experimental evidence is insufficient to characterize pyrrhotite as an HDN catalyst.

1,4-Naphthoquinone: No troilite is observed in the residues; hexagonal pyrrhotite is obtained with 48.1 at.% iron. Results are very similar to the ones obtained for FeS_2.

In the present experiments we have studied the reactions of FeS_2 and Fe_7S_8 with

a selected number of model compounds. From the results of such experiments we suggest that one of the mechanisms by which pyrrhotite enhances coal liquefaction is through interactions with oxygen bonds in coal. There is also evidence from the present experiments as well as those reported in the literature that the pyrrhotites act as hydrogenation catalyst. However, the role of H_2S cannot be completely ignored. There is clear evidence of direct involvement of H_2S in the reactions. The reactions with nitrogen compounds are not very clear and more work remains to be done in this area of research. We are of the opinion that hydrodesulfurization has to be excluded as one of the roles of the pyrrhotites. In the following paragraph we will discuss the behavior of the pyrrhotite surfaces interacting with simple gases.

Electron Energy Loss Measurements

Normal incidence was used for the EEL measurements. The EEL spectra were measured in the second derivative mode for various primary electron energies (50 eV, 150 eV, 250 eV). A small modulation was applied to the CMA (v_{pp}=1 volt) and used as a reference signal. The major impurities were carbon and oxygen. The samples were subjected to Ar^+ ion bombardment for several cycles until a clean surface was obtained.

Electron energy loss spectroscopy is strongly surface sensitive. By varying the electron primary energy one is able to distinguish between volume and surface properties (16). Interband and intraband transitions can be identified with this technique. Ionization losses can be easily studied using electron energy loss spectroscopy. In the present work the major ionization losses studied are the $M_{2,3}$ and M_1 of sulfur and iron.

A. EEL Study of Fe_7S_8 At High Temperatures and in the Presence of CO, O_2 and H_2

Effect of Temperature: The effect of temperature on the EEL spectrum of a single crystal of Fe_7S_8 is shown in Figure 6 (Ep=150eV). One observes the transformation of the EEL spectrum as the temperature is increased, at 320°C there is iron enrichment of the surface. This is detected by the observed enhancement of peak C (surface plasmon of Fe). The peaks J,K are due to a 3p →3d transition ($M_{2,3}$ levels of iron). At 450°C the spectrum of the iron sulfide is different from that observed at RT with B peak shifted in energy from 5.1 to 6.2 eV. The new iron sulfide on the surface has a different electronic structure although some iron character is retained.

Interaction with Co, O_2 and H_2: The Auger spectrum of Fe_7S_8 after reaction with CO (4×10^{-4} torr) at 450°C is shown in Figure 7. One observes the presence of oxygen on the surface. This oxygen is bonded to the iron in the pyrrhotite. This is clearly seen in Figure 8 where the low energy iron Auger peak shows the characteristic shape of the oxide (a strong doublet around 50 eV). No carbon is detected on the surface; the absence of carbon can be explained only by the formation of some volatile species of carbon and sulfur (like CS_2). The electron energy loss spectrum at Ep=150eV is shown in Figure 9. The two strong peaks at low energies are characteristic of the Fe-O system. The Auger spectrum for Fe_7S_8 exposed to O_2 (4×10^{-4} torr, 450°C for five minutes) is shown in Figure 7. One can observe the strong similarities with the spectrum obtained for CO exposure. In Figure 9 the EEL spectrum for oxygen exposure is also shown. There is a great similarity to that of Fe_7S_8 exposed to CO. The lower J,K peak positions and sharpness are characteristic of iron oxides. If hydrogen is used instead of O_2 or CO one obtains the spectrum shown in Figure 9. This spectrum is that of an iron sulfide where some of the sulfur has been removed from the surface. The iron character of the surface is still retained as shown by the presence of the 3p →3d

transitions. If a combination of CO/H_2 (1:1) is used at 450°C the oxygen is totally removed from the surface (formation of H_2O). The iron sulfide surface is restored but with a stoichiometry different from that of Fe_7S_8. In all the experiments described here, a clean Fe_7S_8 sample was used as a starting material. An iron foil doped on the surface with sulfur was also studied using EEL spectroscopy. A very similar spectrum to that obtained at 450°C for Fe_7S_8 was measured. Such a result indicates a strong iron character of the pyrrhotite surface.

B. EEL Study of FeS_2 at High Temperatures and in the Presence of CO, O_2 and H_2

A typical energy loss spectrum of a pyrite single crystal surface is shown in Figure 10 (top). After heating the sample to 220°C one observes a dramatic change in the spectrum. We attribute this change to the presence of elemental sulfur, and probably some $Fe_{1-x}S$. At 320°C the spectrum of the surface is more similar to that of $Fe_{1-x}S$. It is noted that the 3p→3d transitions show the presence of more than two lines. This spectrum for the J,K transitions can be produced by the presence of two iron species ($Fe_{1-x}S$ and FeS_2). At 450°C the surface is that of pyrrhotite with no pyrite character retained. The spectrum is almost identical to that obtained at 450°C from Fe_7S_8 (Figure 7). We want to point out that the high temperature pyrrhotite is not Fe_7S_8.

The behavior of pyrite at 450°C in the presence of CO and O_2 contrasts markedly with that of Fe_7S_8 (see Figures 10 and 11). We believe that this difference in the EEL spectra between the two samples is related to the excess of elemental sulfur present on the pyrite surface at 450°C. This excess of sulfur does not permit the iron in the pyrrhotite to react with CO or oxygen. If H_2 is used as a gas instead of CO or O_2 a small change is observed in the EEL spectrum, probably due to the removal of the sulfur from the surface. If a combination of CO/H_2 (1:1) is used in the reactor, an EEL spectrum very similar to that observed for Fe_7S_8 is obtained. In this case elemental sulfur is removed from the surface and the surface behaves as that of a pure pyrrhotite.

In conclusion we find that the major difference in the behavior of the pyrrhotite and pyrite surfaces at high temperature is due to the presence of an excess of sulfur on the latter. We also observe that the pyrrhotite surface has a strong iron character and great affinity to oxygen. Although the present study is only on very simple gases, these gases are present in the reactor during direct coal liquefaction.

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Table I

ISOMER SHIFT AT 420 °C

Sample	I.S. ($mmsec^{-1}$) (at 420 °C)
IL6	0.38 ± 0.05
KY 9/14	0.34 ± 0.05
Powhatan 5	0.35 ± 0.05
Blacksville #2	0.21 ± 0.05
Fe_7S_8	0.50 ± 0.03
FeS	0.51 ± 0.05

TABLE III

Compositions of the residues obtained from Fe_7S_8 + H_2 + model compounds

Dibenzothiophene	$Fe_{1-x}S$	(25%) : at.% Fe	48.2 ± 0.1
	FeS	(75%)	
Pyrene	$Fe_{1-x}S$	(11%): at.% Fe	48.2 ± 0.1
	FeS	(89%)	
Phenanthrene	$Fe_{1-x}S$	(23%): at.% Fe	47.7 ± 0.1
	FeS	(77%)	
1,4 Naphthoquinone	$Fe_{1-x}S$	(100%): at.% Fe	48.1
Phenothiazine	$Fe_{1-x}S$	(100%): at.% Fe	47.6
Quinoline	$Fe_{1-x}S$	(100%): at.% Fe	48.2

TABLE II

Mössbauer Parameters

COMPOUND	IS mm/s T=440°C	FeS_2 + N_2 QS mm/s T=440°C	RESIDUES at RT	IS mm/s T=440°C	FeS_2 + H_2 QS mm/s T=440°C	RESIDUES at RT
Dibenzothiophene	~ 0.0	0.63 ± 0.1	$Fe_{1-x}S$ at.%Fe 46.8	0.36 ± 0.05	-	$Fe_{1-x}S$ at.%Fe 48.2
Pyrene	~ 0.0	0.57 ± 0.1	FeS_2 (47%) $Fe_{1-x}S$(53%) at.% Fe 46.8	0.35 ± 0.05	-	at.%Fe 47.8
Phenanthrene	~ 0.0	0.45 ± 0.1	FeS_2 (24%) $Fe_{1-x}S$(76%) at.%Fe 46.8	0.50 ± 0.05		at.%Fe 48.1
1,4 Naphthoquinone	~ 0.04	0.57 ± 0.05	FeS_2 (70%) Fe_3O_4 $Fe_{1-x}S$ 46.7 at.%Fe	0.02 ± 0.05	0.53 ± 0.05	$Fe_{1-x}S$ at.% Fe 48.0
Phenothiazine	~ 0.04 ± 0.05	0.58 ± 0.05	FeS_2 (82%) $Fe_{1-x}S$ (18%) 46.8 at.%Fe	0.0	0.61 ± 0.05	FeS_2 (17%) $Fe_{1-x}S$ (83%)
Quinoline	~ 0.03 ± 0.05	0.56 ± 0.05	FeS_2 (73%) $Fe_{1-x}S$(27%) 46.7 at.%Fe	0.0	0.55 ± 0.05	FeS_2(64%) $Fe_{1-x}S$(26%) at.% Fe 47.8

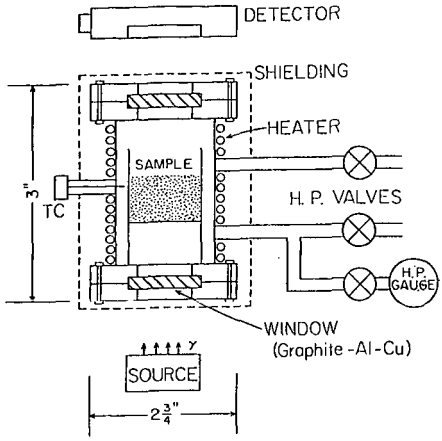

FIGURE 1 Reactor for Mössbauer "in-situ" measurements.

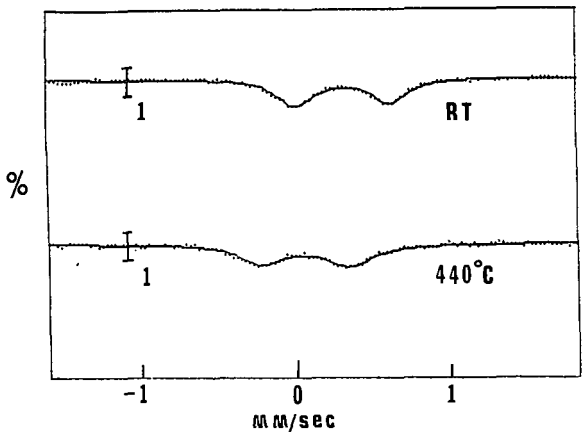

FIGURE 2 Mössbauer spectra at RT for a mixture of FeS_2 and DBZ.

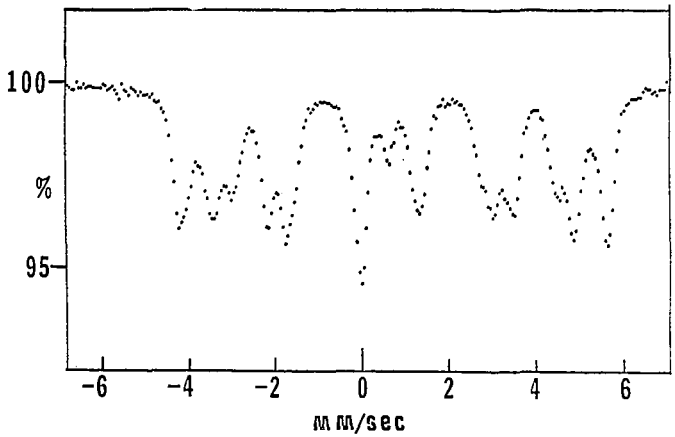

FIGURE 3 Mössbauer spectra at RT of the residue of the reaction of FeS_2 and DBZ.

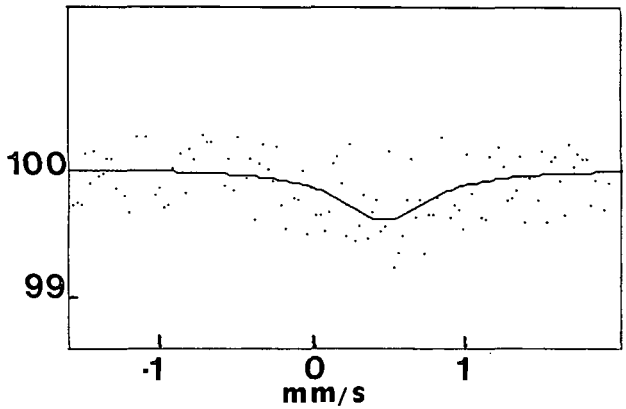

FIGURE 4 Mössbauer spectra at 450°C of Fe_7S_8 and pyrene in a hydrogen atmosphere.

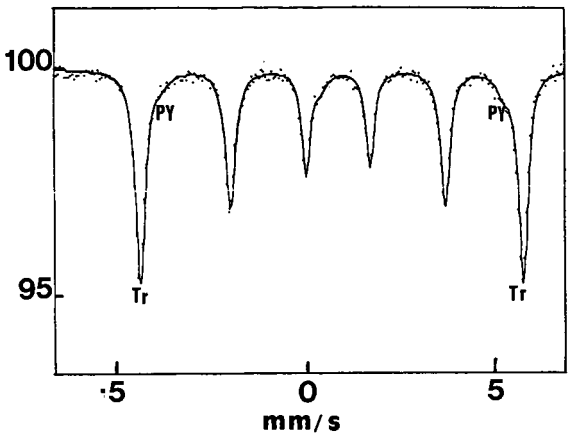

FIGURE 5 Mössbauer spectra of the residue of the reaction of Fe_7S_8 with pyrene. Tr: troilite
Pr: pyrrhotite

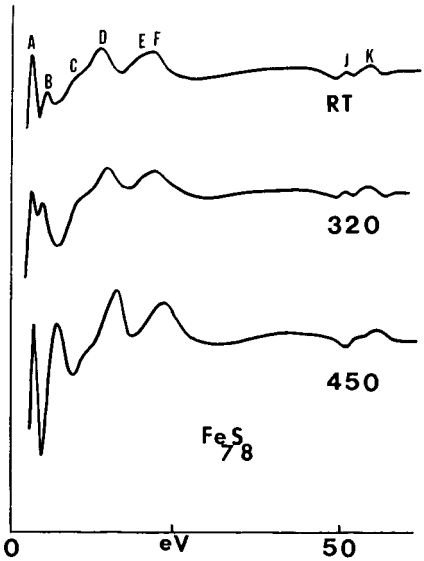

FIGURE 6 EEL spectra of Fe_7S_8 at various temperatures.

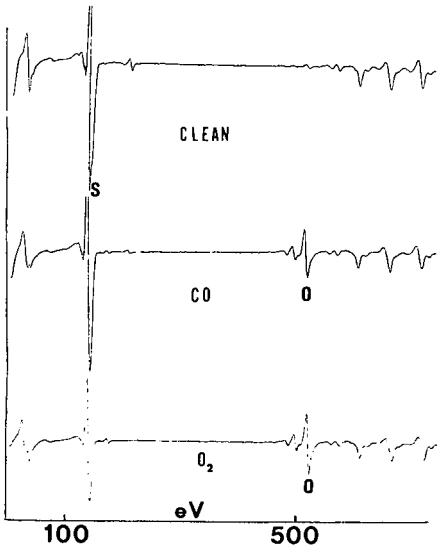

FIGURE 7 Auger spectra of Fe_7S_8 after a reaction with CO and O_2.

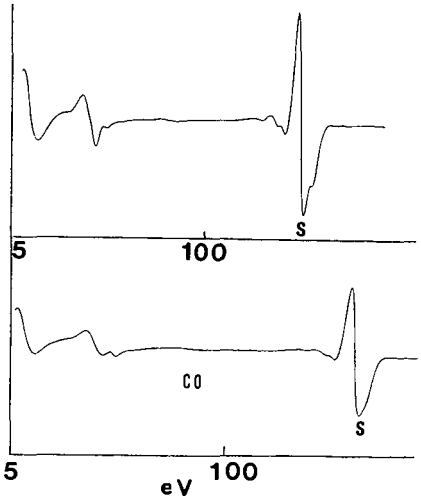

FIGURE 8 Auger spectra of Fe_7S_8 at low energies, clean and in the presence of CO (450° C).

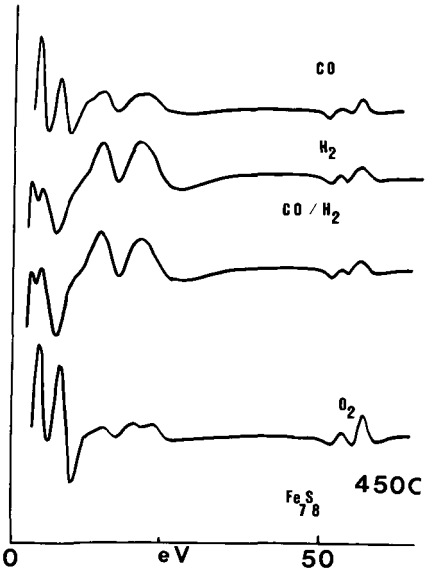

FIGURE 9 EEL spectra of Fe_7S_8 after reactions at 450° C with CO, H_2 and O_2.

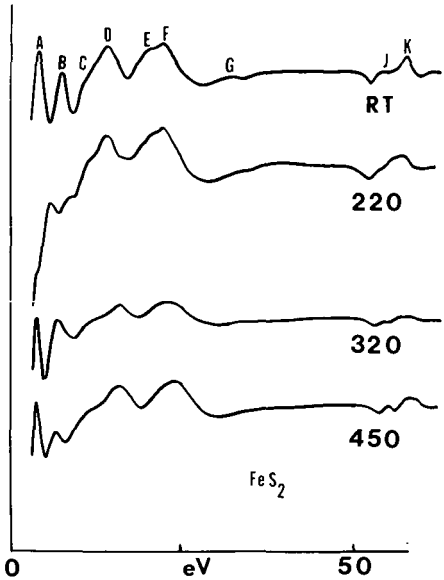

FIGURE 10 EEL spectra of FeS_2 after heating to various temperatures (RT to 450° C).

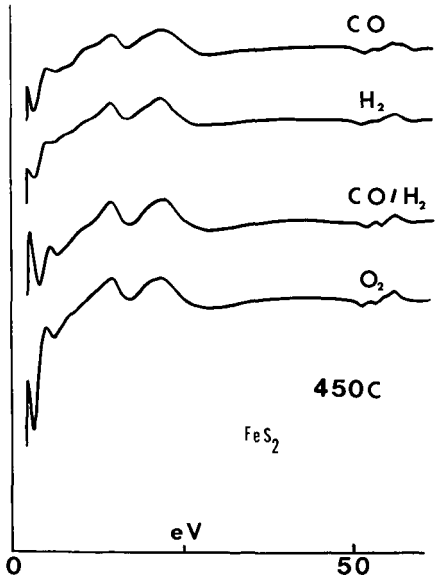

FIGURE 11 EEL spectra of FeS_2 after reaction with CO, H_2 and O_2 at 450° C.