MÖSSBAUER INVESTIGATION OF MATERIALS USED IN SANDIA'S DCL CATALYST TESTING PROGRAM

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ABSTRACT

Mössbauer spectroscopy has been used to determine the iron-bearing phases in the coal, catalysts, and IOM products used and generated in the Direct Coal Liquefaction (DCL) catalyst testing program at Sandia National Laboratories, New Mexico. DCL experiments were conducted with a Blind Canyon, Utah, coal both thermally and with three different iron-based catalysts: (i) a sulfated hematite catalyst (Fe_2O_3/SO_4^{2-}), (ii) a 6-line ferrihydrite catalyst, and (iii) iron-oxide impregnated directly into coal. The catalysts were added to the coal at both a 0.5 and a 1.0 wt% level and sufficient sulfur was added to ensure complete sulfidation of the iron. The Mössbauer spectrum of the Blind Canyon coal revealed that the major iron-bearing mineral present was ankerite, $Ca(Fe,Mg)(CO_3)_2$, which converts first to γ-Fe (austenitic iron) before undergoing partial sulfidation to pyrrhotite in the thermal runs. The percentages of pyrrhotite formed in the catalytic runs were higher than those in the thermal runs indicating that sulfidation of the added iron occurs more rapidly than with the ankerite. Mössbauer data on the amount of pyrrhotite present does not correlate well with THF and heptane conversion percentages, indicating that other parameters like catalyst dispersion must also be considered.

INTRODUCTION

It is well recognized that iron-based materials represent the best option for development of a low-cost, disposable catalyst for direct coal liquefaction (DCL) [1]. As a result, much effort has been recently directed towards the development of iron-oxide-based catalysts for DCL by many groups [2]. However, owing to differences in DCL testing procedures at different laboratories, it has not always been possible to compare directly the conversion and cost effectiveness of different catalyst formulations. The DCL catalyst testing program at Sandia National Laboratories was designed to resolve such uncertainties by providing a facility for the DCL research community where the effectiveness of different catalysts could be directly compared [3]. Each catalyst would be subjected to the same matrix of tests on the same coal (Blind Canyon, UT, DECS-17) under identical conditions and the analysis of the DCL products would also be standardized.

In the current study, Mössbauer spectroscopy has been used to characterize the iron in various starting materials and products from the Sandia DCL program in order to provide additional baseline information for the program. Mössbauer investigations have been carried out on the following materials:

A. (1) Blind Canyon Coal (DECS-17)

   (2) A sulfated hematite catalyst, Fe_2O_3/SO_4^{2-}, from the University of Pittsburgh

   (3) A 6-line ferrihydrite catalyst from Pacific Northwest Laboratories

   (4) An iron-oxide based catalyst impregnated into Blind Canyon Coal from West Virginia University

B. THF-insoluble residues generated in thermal liquefaction runs at 350°C for 20 min and at 400°C for 60 min.

C. THF-insoluble residues generated in liquefaction runs with the sulfated hematite catalyst at:

350°C	20 min	1.0 wt% catalyst loading and 1 wt% sulfur
375°C	40 min	0.5 wt% catalyst loading and 1 wt% sulfur
400°C	60 min	1.0 wt% catalyst loading and 1 wt% sulfur

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D. THF-insoluble residues generated in liquefaction runs with the ferrihydrite catalyst at:

350°C	20 min	1.0 wt% catalyst loading and 1 wt% sulfur
375°C	40 min	0.5 wt% catalyst loading and 1 wt% sulfur
400°C	60 min	1.0 wt% catalyst loading and 1 wt% sulfur
400°C	60 min	1.0 wt% catalyst loading and 2 wt% sulfur

E. THF-insoluble residues generated in liquefaction runs with the iron-oxide catalyst impregnated in Blind Canyon Coal at:

350°C	20 min	1.0 wt% catalyst loading and 1 wt% sulfur
400°C	60 min	1.0 wt% catalyst loading and 1 wt% sulfur

EXPERIMENTAL

The thermal and catalytic DCL experiments were carried out under 800 psig H_2 in microreactors at Sandia National Laboratories with the above catalysts and sufficient sulfur to ensure complete sulfidation of the iron [3]. Oil and total conversions, defined as the percentages of the sample after DCL that were soluble in heptane and tetrahydrofuran, respectively, were also determined at Sandia [3]. Samples of the residues and starting materials were shipped to the University of Kentucky for Mössbauer analysis. Mössbauer analysis was carried out using a Halder, GmbH, Mössbauer drive operating in the symmetric saw-tooth mode. A calibration spectrum of metallic iron was obtained at the opposite end of the drive at the same time as the unknown spectrum was being acquired. Each spectrum was acquired over 512 channels representing a velocity range of between ±8 and ±12 mm/s using Canberra/Nuclear Data multichannel scaling units located in 286DX personal computer. Spectra were obtained from all samples at room temperature and from a few samples at cryogenic temperatures as low as 13 K. Analysis of the Mössbauer spectra was conducted in the manner described previously [4,5]. Spectra were fit by means of a least-squares fitting routine as a combination of 6-line magnetic spectra, 2-line quadrupole doublets and single lorentzian-shaped peaks. Identification of the iron-bearing phases present in the samples was based solely on the values obtained for the isomer shift, quadrupole splitting, and magnetic hyperfine splitting_ of the individual components in the fits. The relative percentages of iron present in the different phases were derived from the areas under the individual components. Mössbauer results for the thermal and catalytic residues from the DCL tests are summarized in Tables I - III for the three different catalysts.

RESULTS AND DISCUSSION

The Mössbauer spectrum of Blind Canyon (DECS-17) coal is shown as Figure 1. The spectrum consists of one major doublet from which the principal iron-bearing mineral in the coal is identified as ankerite, $Ca(Fe,Mg)(CO_3)_2$. It has the same isomer shift (1.23±0.01 mm/s), but a significantly smaller quadrupole splitting (1.67±0.02 mm/s) than that reported [4] for siderite (1.80±0.02 mm/s). Although no positive evidence was established for the presence of pyrite in this coal, it is possible that as much as 5% of the iron could be present as FeS_2. This minor contribution cannot be resolved owing to the overlap of the low-velocity ankerite peak with the pyrite peaks coupled with the relatively poor signal/noise ratio as a result of the low iron content of this particular coal.

Essentially the same results were obtained with the three thermal runs at the two different temperatures. In the thermal residues prepared at 350°C, ankerite, and austenitic or γ-iron were observed; at 400°C (q.v. Figure 2), significant pyrrhotite ($Fe_{1-x}S$), in addition to ankerite (with a smaller quadrupole splitting, 1.52 mm/s, than was found at 350°C) and γ-Fe, was also observed. These observations imply that ankerite in the coal reduces partially to γ-Fe, which then reacts with sulfur to form pyrrhotite.

The Mössbauer spectra of the sulfated hematite consisted of a magnetic component attributed to hematite and a poorly resolved doublet that represents the sulfated surface of the hematite particles and/or superparamagnetic (spm) iron oxide particles of small size (less than about 10 nm [5]). The other two catalysts exhibited only a broad doublet in their Mössbauer spectra; such spectra are consistent with ferrihydrite, either as a separate phase [6,7] or formed by impregnation directly on the coal [7].

The Mössbauer spectra of the catalytic residues (e.g. Figure 3) were similar to each other for the most part. However, the residues from the ferrihydrite and impregnated catalysts did show the persistence of a doublet attributed to unreacted spm iron oxides that was not apparent with the sulfated hematite catalyst. The relative amount of pyrrhotite

Table I

Mössbauer analysis of iron-bearing phases in
THF insolubles from thermal and catalytic reactions
with a sulfated hematite catalyst and Blind Canyon Coal

Sample	Gamma-Fe	Ankerite	Pyrrhotite
350, 20 min, thermal	14	86	
350, 20 min, 1 wt%	26	33	41
375, 40 min, 0.5 wt%	16	33	51
400, 60min, thermal	20	37	43
400, 60 min, 1 wt%	10	21	69

Table II

Mössbauer analysis of iron-bearing phases in
THF insolubles from thermal and catalytic reactions of
with a 6-line ferrihydrite catalyst and Blind Canyon Coal

Sample	γ-Fe	Ankerite	Pyrrhotite	FeOOH/Oxide
As received 6-line ferrihydrite				100 FeOOH
350, 20 min, thermal	13	87		
350, 20 min, 1 wt%	6	28	42	24
375, 40 min, 0.5 wt%	8	25	57	10
400, 60 min, thermal	18	36	46	
400, 60 min, 1 wt%	1	13	68	18
400, 60 min, 1 wt% 2 wt% added sulfur	10	18	67	5

Table III

Mössbauer analysis of iron-bearing phases in
THF insolubles from thermal and catalytic reactions
with iron-oxide impregnated Blind Canyon Coal

Sample	γ-Fe	Ankerite	Pyrrhotite	FeOOH/Oxide
Coal impregnated with iron and sulfur compounds		31		69
350, 20 min, thermal	23	77		
350, 20 min, 1 wt% catalyst in coal	25	25	31	19
400, 60 min, thermal	15	36	49	
400, 60 min, 1 wt% catalyst in coal	5	16	51	28

formation in all three catalytic runs was greater than that in the corresponding thermal run at the same temperature indicating that the iron-based catalyst undergoes sulfidation much more rapidly than the ankerite in the original coal.

The THF conversions for the catalytic runs at 400°C, 60 min, with 1% loading for the sulfated hematite, 6-line ferrihydrite, and impregnated iron-oxide catalysts were 82.3%, 89.4% and 93.2%, respectively. These values do not show a direct correlation with %Fe as pyrrhotite listed in Tables I - III, but do correlate with %Fe remaining as spm oxide.

CONCLUSIONS

Iron in Blind Canyon coal (DECS-17) is present principally in the form of ankerite, $Ca(Fe,Mg)(CO_3)_2$, which is converted during thermal tests, first to γ-Fe and then to pyrrhotite. The conversion is not complete even after 60 mins at 400°C. In contrast, sulfidation of the catalyst materials is more rapid and is essentially complete in the case of the sulfated hematite catalyst at 350°C and nearly so in the case of the 6-line ferrihydrite and impregnated iron-oxide catalysts. With the latter two catalyst materials, a small fraction (up to 25%) of the catalyst persists as spm iron-oxide even to the most severe conditions employed for DCL (400°C, 60 min). It is this fraction of iron present as remnant spm iron-oxide, and not as pyrrhotite, that appears to show a direct correlation with the total DCL conversion percentages. This observation implies that there are significant differences in the ease of sulfidation of the iron-oxides to form pyrrhotite among the three catalysts that are also reflected in the dispersion and size of the pyrrhotite particles. It is these parameters that may have the most influence on the activity of the sulfided iron catalyst during the DCL process.

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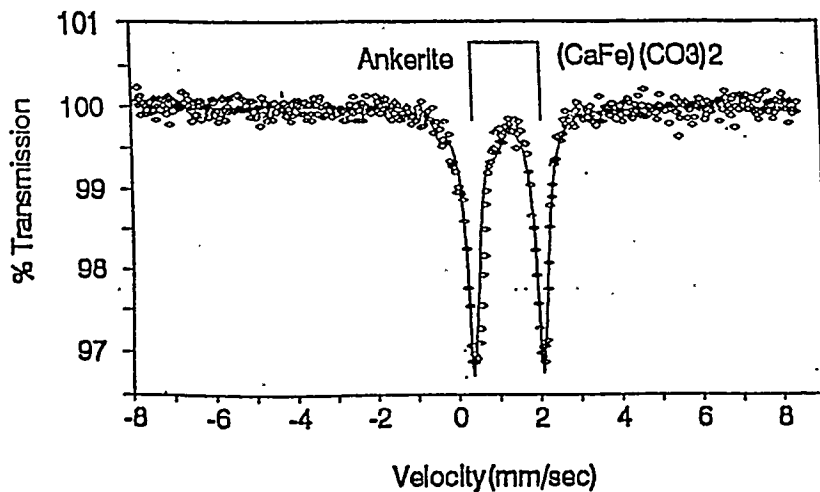
ACKNOWLEDGEMENTS

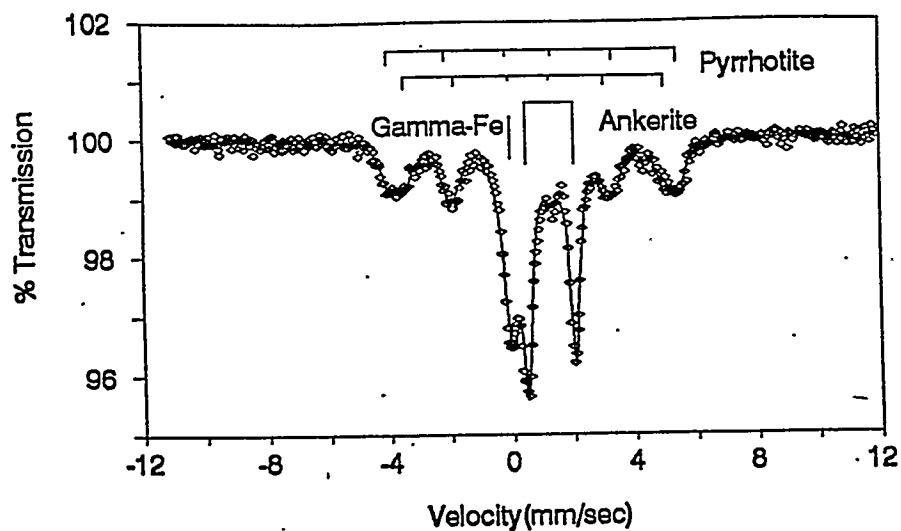**Fig.1 Mossbauer spectrum of Blind Canyon Coal**

Fig.2 Mossbauer spectrum of THF Insoluble from the run at 400C, 60min, without any catalyst (thermal)
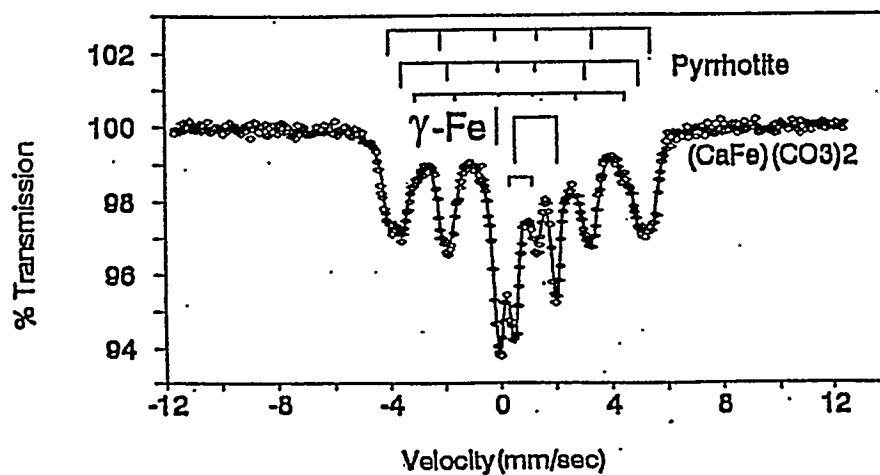

Fig.3 Mossbauer spectrum of THF Insoluble from the run at 400C, 60min with Wender's 1% catalyst