

# **TASK I**

## **Project I.3**

### **GENERIC STRUCTURAL CHARACTERIZATION AND LIQUEFACTION RESEARCH**

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#### **Introduction**

This project consists of both a structural characterization component and a component which deals with the synthesis, testing, and characterization of novel iron-based catalysts. Studies were also initiated near the end of the year of the coliquefaction of coal with plastics. These results of these various research components are summarized in sections I.3.1-I.3.4 below.

#### **I.3.1 GENERIC STRUCTURAL CHARACTERIZATION RESEARCH**

Excellent progress was made in developing accurate methods of characterizing the size and structure of iron-based catalysts. The methods used were Mossbauer spectroscopy, XAFS spectroscopy, and transmission electron microscopy. Most of the results have summarized in a number of recent and forthcoming publications,<sup>(1-5)</sup> and will not be repeated here. One of the current authors (Bhaswati Ganguly) completed her Ph.D. in physics in the current year; her thesis title was, "Mossbauer Studies of Iron-Based Ultrafine Coal Liquefaction Catalysts."

In addition to carrying out the basic research required to establish structural characterization methodology, we have also investigated numerous catalysts from other CFFLS groups and other groups involved in iron catalyst development in the DOE AR&TD program. These results have been reported directly to the investigators responsible for synthesizing the catalysts and some of them are discussed in other sections of this report.

## References

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5. "Determination of the Size of Iron Oxide Catalysts from Superparamagnetic Mossbauer Relaxation Spectra," B. Ganguly, F.E. Huggins, K.R.P.M. Rao, and G.P. Huffman, *J. of Catalysis*, **1993**, *142*, 552-560.

## **I.3.2 LIQUEFACTION OF LOW-RANK COAL CONTAINING CATION-EXCHANGED IRON**

### **Introduction**

Catalyst particle size has a strong effect on catalytic activity and selectivity during direct coal liquefaction. Fine particles are desirable because the majority of the atoms are coordinatively unsaturated and have a large percentage of surface sites that are readily accessible for chemisorption and catalysis. Ion-exchange procedure plays a very important role in many chemical processes, because of its simplicity, selectivity, and finally its wide scope. Ion-exchange in which an ion in coal such as calcium is replaced by a catalytic ion such as iron can yield an ultrafine particle size with an even distribution of catalytic ions. This constitutes a new class of catalyst stabilized in a state of high dispersion even at coal liquefaction conditions. The work during this period focused on investigation into the role of ion-exchanged iron during direct coal liquefaction (DCL) of two lignites and a subbituminous coal. The results indicate that iron ion-exchanged into the low-rank coals constitutes a catalyst in a state of dispersion ranging from molecular ions to particles a few nanometers in diameter<sup>1, 2</sup>.

### **Experimental**

The coals used in this study are Beulah lignite (obtained from Department of Energy Coal Samples, DECS-11) and Hagel lignite (obtained from Penn. State Office of Coal, PSOC-1482) from the Fort Union region in North Dakota, and a subbituminous Black Thunder coal. The original iron contents of these coals are less than 0.5 percent. The coal samples were first ground to <200 mesh under a nitrogen atmosphere. The ion-exchange experiments were carried out in a 10 liter fermenter equipped with temperature and pH controllers. A freshly made 0.05M aqueous solution of ferric acetate was kept at a controlled pH of about 2.8 using sulfuric acid and a constant temperature of 333K. A slurry made from a 10:1 ratio by weight of dry coal to ferric acetate was stirred under a nitrogen atmosphere for 20 hrs. At the completion of the procedure, the ion-exchanged coals were repeatedly washed with

distilled water until the pH value of the filtrate for two consecutive washes was constant. The iron contents of the Beulah and Hagel lignites and Black Thunder coal after the ion-exchange process were 7.8%, 5.33%, and 3.8%, respectively. The efficiency of lower loadings of iron in the ion-exchanged coals during liquefaction was also investigated; samples of the same lignites were first demineralized in a manner similar to the procedure described by Bishop and Ward<sup>3</sup> and then ion-exchanged to final iron contents of 0.93% for Beulah, and 0.88% for Hagel lignite.

### **Liquefaction Experiments**

Two sets of coal liquefaction experiments were conducted. The first set of experiments was carried out with tubing bombs in a fluidized sand bath. This set of experiments was designed to investigate the effect of ion-exchanged iron catalysts on the total yield and product distribution in the liquefaction process. Control liquefaction experiments, using slurry mixtures of the same coal samples with a 30Å iron oxide (ferrihydrite) and with no catalyst, were run under the same conditions. The second set of experiments was designed to generate larger samples for the detailed characterization of the chemical structure and reactions of the added iron. The apparatus used to prepare the samples for these experiments was a one liter autoclave. This autoclave was connected at the top to a vessel for holding the sample prior to heating. At the bottom, four nitrogen-purged sampling lines were attached to the outlet valve of the autoclave to collect the liquefaction products directly from the autoclave without exposure to air. Liquefaction experiments were performed in the presence of excess tetralin and dimethyl disulfide (DMDS) as a sulfur donating species.

### **Mössbauer and XAFS Spectroscopy**

Mössbauer spectra for the as-received, demineralized, and ion-exchanged coal samples were obtained using a conventional constant-acceleration-type Mössbauer spectrometer<sup>4</sup>. Calculation of the particle size distribution is described in detail elsewhere<sup>5</sup>. XAFS measurements were performed at beam line X-19A at the National Synchrotron Light Source in Brookhaven National Laboratory. Iron K-edge XAFS

spectra of the samples were obtained in transmission mode using a Si(111) double crystal monochromator.

## Results and Discussion

The total conversion and product distribution of oils, asphaltenes, and preasphaltenes for Beulah, Hagel lignites, and Black Thunder coal from the tubing bomb liquefaction experiments at 673K for 60min are illustrated in Figure 1(a, b, and c). It can be seen that the asphaltene and oil conversion yields increased significantly for all ion-exchanged coals, with a sulfur donating species (DMDS) present. The preasphaltene yields, however, tend to decrease as a result of iron species incorporated into the coal. The variation in the product yields with the addition of a catalyst may be related to the conversion of preasphaltene and asphaltene as the reaction proceeds. It is evident from Figure 1 that the ion-exchanged iron is a more active catalyst than the 30Å ferrihydrite. Both the total conversion and the oil yield are substantially greater for the ion-exchanged iron than the 30Å catalyst at approximately the same concentrations. Elemental analyses of all three coals before and after the ion-exchange process indicate that the calcium content of these samples decreased by about 1.2% after treatment, while the concentration of other alkali and alkaline earth cations remains more or less constant. Thus, iron in ion-exchange process was exchanged primarily for calcium, yielded a highly dispersed catalytic iron species for coal liquefaction. Joseph et al.<sup>6</sup> have shown that calcium decreases the conversion yields of coal during DCL.

Typical Mössbauer spectra of a coal containing cation-exchanged iron are shown in Figure 2. The spectra are fit with one or several magnetic components and quadrupole doublets (peak positions denoted by bar diagrams), and a superparamagnetic relaxation component (dashed curve). As discussed by Ganguly et al.<sup>5</sup>, at a given temperature, particles with diameter less than some critical value will give rise to a quadrupole doublet, particles with a diameter greater than some larger critical value will exhibit a six-peak magnetic hyperfine spectrum, and particles with diameters between these two values will give rise to superparamagnetic spectra. Approximate size distributions can be determined by

measuring the percentages of these three components as a function of temperature. A typical size distribution determined in this manner for the cation-exchanged Beulah lignite for two different iron contents is shown in Figure 3. It is seen that the size distribution is bimodal, with a significant fraction of the iron in particles finer than 30Å in diameter and highly dispersed particles in the 30-100Å size range. In addition, the size distribution patterns of the low-iron-content cation-exchanged coals indicate the formation of the fine (less than 30Å) iron-bearing fraction in larger relative amounts. These observations imply that there are two distinct forms of iron present in these samples. The iron in the finer particle size (less than 30Å) category may in fact be ferric iron that is molecularly dispersed and bonded to oxygen anions of the carboxyl groups in the coal, while particles in the 30-100Å size range result from hydrolysis and agglomeration of either iron acetate or ion-exchanged iron to form larger iron oxyhydroxide particles.

Both the x-ray absorption near edge structure (XANES) and the radial structure function (RSF) derived from the iron K-edge XAFS spectra of the cation-exchanged coals exhibit significant size related effects. Typical results are shown in Figure 4. The XANES of cation-exchanged coals (Hagel with 5.33% and 0.88% iron content) are compared to that of bulk iron oxyhydroxide ( $\alpha$ -FeOOH) in Figure 4a, while the corresponding RSF are compared in Figure 4b. It is seen that the XANES of the cation-exchanged iron and goethite are quite similar, with the exception of an increase in the intensity of the small pre-edge peak. This occurs because a significant fraction of the iron atoms in the coals is no longer in centrosymmetric octahedral coordination, but in reduced coordination number sites, which causes the intensity of the pre-edge ( $1s \rightarrow 3d$ ) transition to increase<sup>7</sup>. This is believed to be due to surface iron atoms in the goethite particles and/or to carboxyl-bound iron atoms. The RSFs of the cation-exchanged iron in coals and iron in goethite exhibit similar peaks, but the peaks corresponding to the iron shells are decreased in amplitude for the iron in the coal. During DCL most of the cation-exchanged iron reacts with  $H_2S/H_2$  to form pyrrhotite. In most cases, however, a small iron oxide remnant remains.

## References

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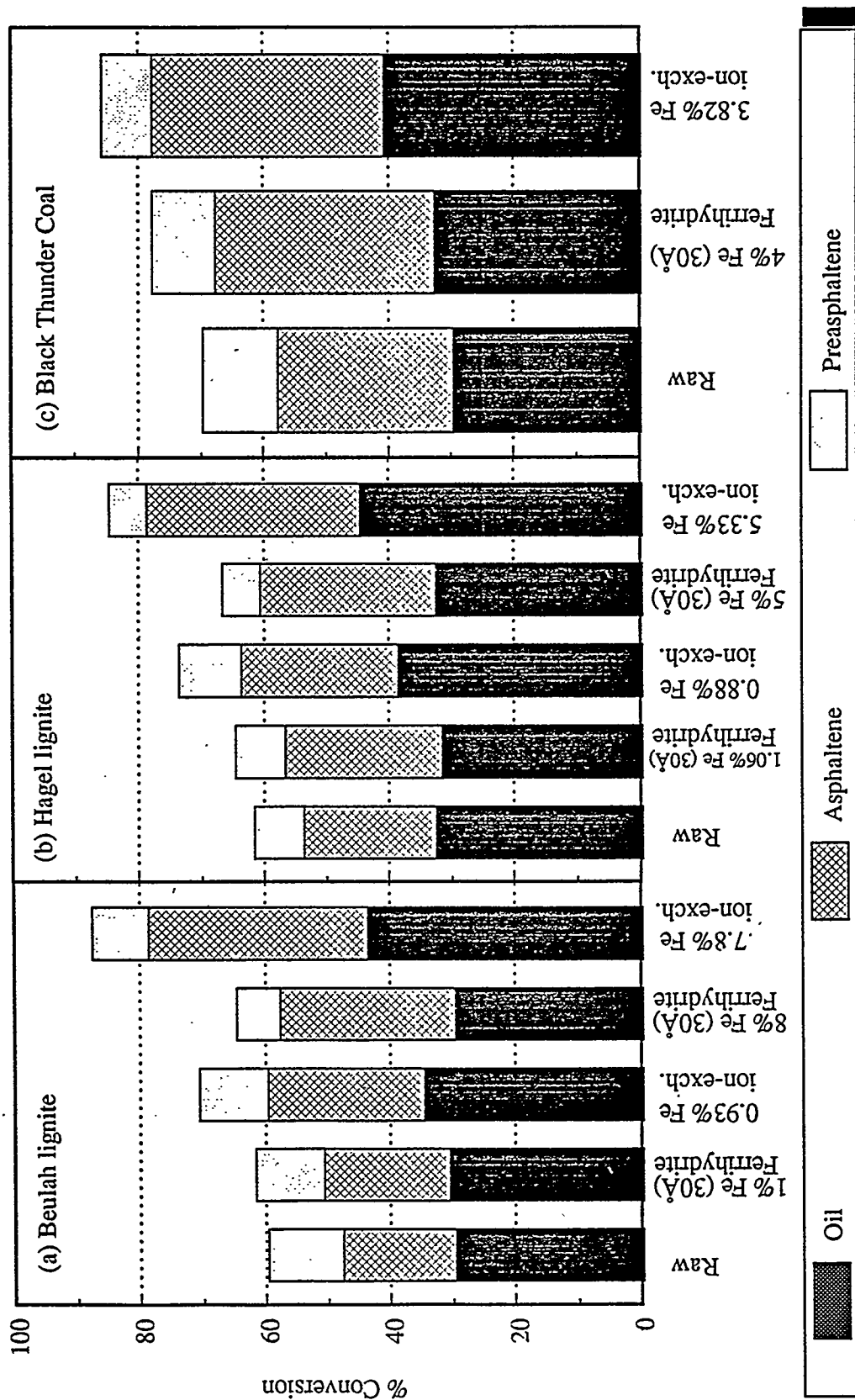


Figure 1. Comparison of liquefaction product yield for Beulah, Hagel lignites and Black Thunder coal.



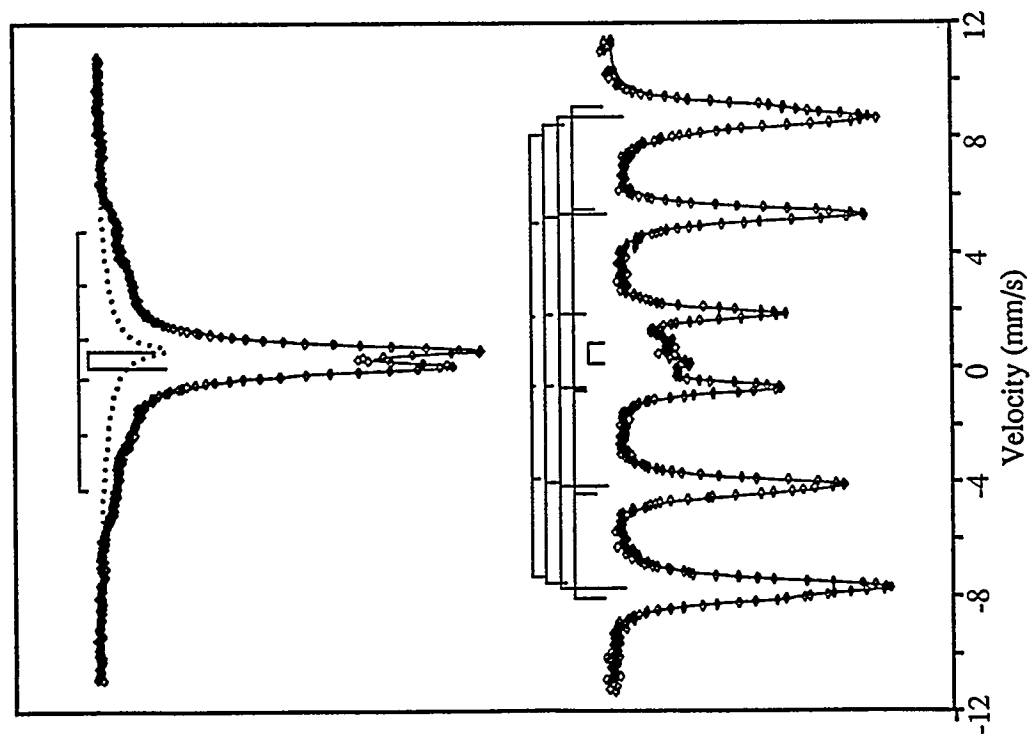


Figure 2. Mossbauer spectra of iron ion-exchanged Beulah lignite at room temperature and at 12K.

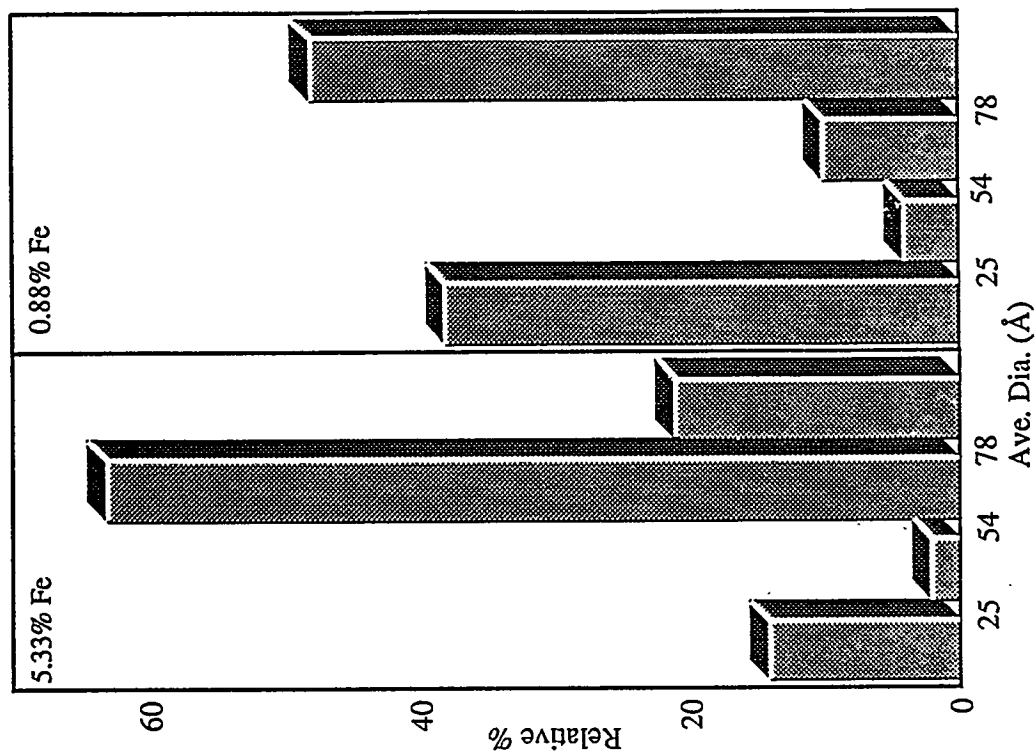


Figure 3. Size distribution of iron ion-exchanged Beulah lignite with indicated iron percentages.

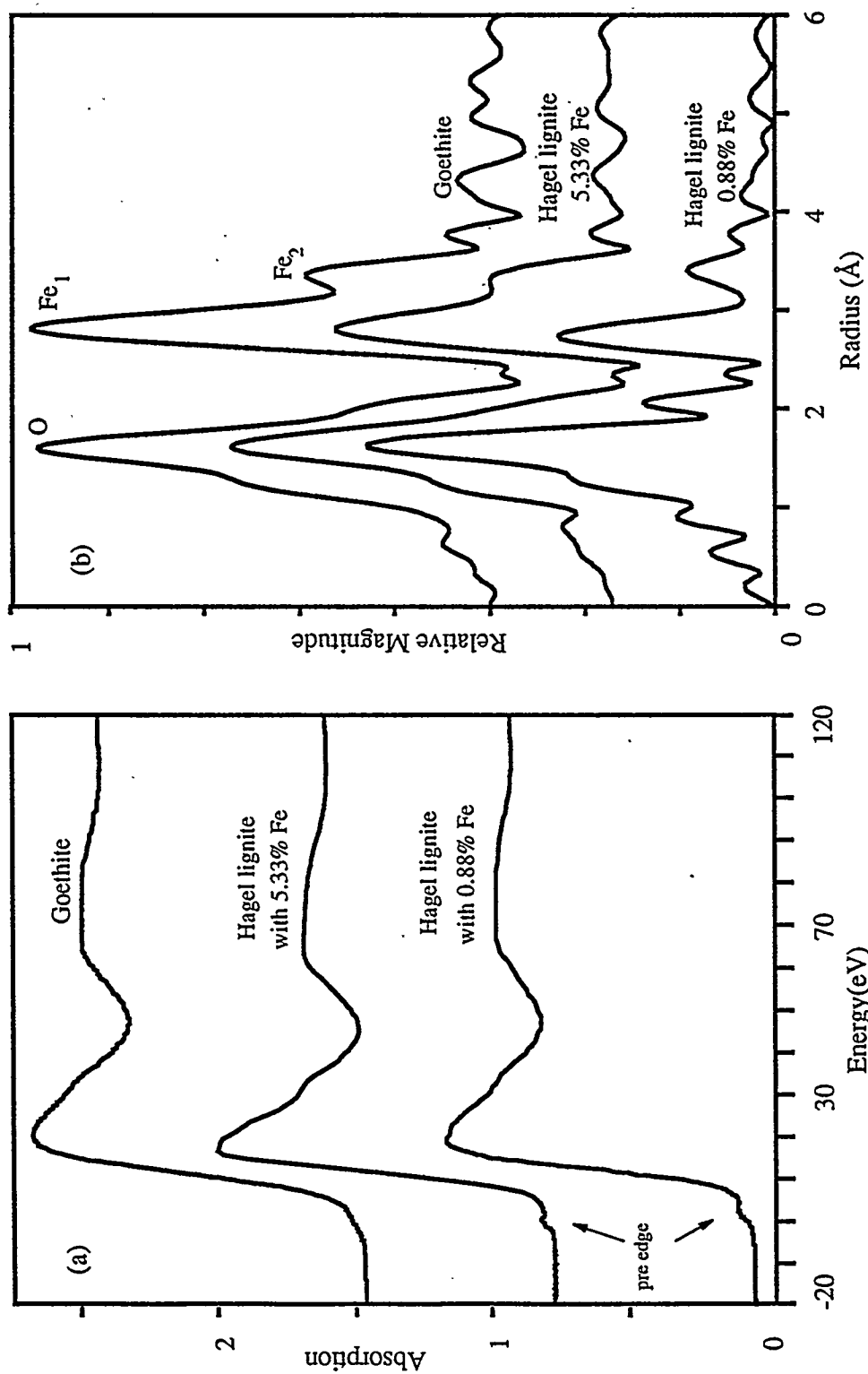


Figure 4. Comparison of (a) x-ray absorption near edge structure (XANES), and (b) radial structure function (RSF) of FeOOH and ion-exchanged Hegal lignite.

### **I.3.3 DEVELOPMENT OF BINARY FERRIHYDRITE CATALYSTS FOR DIRECT COAL LIQUEFACTION**

Because of its unique small particle size and large surface area, the 30Å NANOCAT™ catalyst manufactured by Mach I, Inc. has attracted much attention among the researchers in the consortium. The work conducted by our group is summarized below:

#### **1. Structure of the 30Å catalyst**

The 30Å catalyst is actually ferrihydrite which is one of the eight major iron oxide/oxyhydroxide phases. The structure of ferrihydrite is still controversial. Using X-ray absorption fine structure (XAFS), we found that the structure is oxyhydroxide-like with iron octahedrally coordinated by oxygens and oxyhydroxy groups. Of more significance, a large percentage of surface iron ions are at coordinate unsaturated (CUS) sites with tetrahedral symmetry. Figure 1 shows the proposed structure.

#### **2. Agglomeration and phase transition of the 30Å catalyst (ferrihydrite).**

The iron oxide catalysts are in fact the catalyst precursor for coal liquefaction. Under reaction conditions, the catalyst may experience several stages of phase transformation before converting to  $\text{Fe}_{1-x}\text{S}$  phase. One major concern for the iron catalysts is whether they are able to maintain their dispersion under reaction conditions. At high temperature ferrihydrite decomposes to hematite. TEM micrographs show that the 30Å catalyst after annealing at temperatures between 250 - 350°C contains two phases, a hematite phase with large particle size ( $d > 200\text{Å}$ ) and small, apparently unaltered 30Å particles. Substantially more and larger hematite particles are observed if the samples has been exposed to moisture in the air for several day prior to annealing [2]. The phenomenon can be interpreted on the basis of surface structure. Upon exposure to moisture, water molecules are chemisorbed at the catalyst surface and the small particles become linked by the chemisorbed water. At high temperature, these water molecules are detached from the particle joints, causing agglomeration of small particles and formation of  $\alpha\text{-Fe}_2\text{O}_3$  phase with decreased surface area. Detailed papers have been prepared discussing both the structure [1] and the agglomeration and phase transition of the catalyst during

annealing.

### 3. Synthesis and characterization of the binary ferrihydrite catalysts

Since the CUS sites can adsorb water molecules, they may adsorb a second element (M) if it is present during precipitation, forming M-O-Fe species at the catalyst surface. With chemisorbed water molecules, the CUS sites become the crystal growth sites; but once the CUS sites are occupied by the second element, the crystal growth sites become blocked (Figure 2), and the catalyst may be able to maintain its dispersion at high temperatures.

We have succeeded in synthesizing a series of binary ferrihydrite catalysts by coprecipitating Al, Si, Zn, and Mo with ferric nitrate. The average particle sizes of the catalysts determined by TEM micrographs are 30 - 100Å. XRD, Mossbauer spectroscopy and XAFS results show that the catalysts are structurally identical to the 30Å catalyst. TEM micrographs of the catalysts show that the nanoscale particles are heavily aggregated, whereas the 30Å catalyst particles are well separated.

To examine the effect of the second component on catalyst agglomeration, the catalysts were annealed at 400°C for 5 hours in air, and the structure of the samples before and after annealing were examined by XRD. Figures 3 and 4 show the results for pure ferrihydrite, and the ferrihydrite catalysts with 5% Mo, 5% Si, and 50% Al.

Among the compounds used as second components for coprecipitation with ferric nitrate, SiO<sub>2</sub> is most effective in preventing catalyst agglomeration. With Si/Fe = 5%, no  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase was seen after annealing at 400°C for 5 hours in air (Figure 4).

With 5% of Mo, Al and Zn added to the ferric nitrate solution, crystalline  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was observed after annealing. The particle sizes of the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> phase estimated from the width of the XRD peaks are considerably smaller than that of pure ferrihydrite (30Å). No formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> was seen with Al/Fe = 50%.

### 4. Coal liquefaction test results.

Preliminary direct coal liquefaction tests have been performed using a tubing bomb. The conditions and product analysis are shown in Table 1. The results show that the binary catalysts are as good as or better than the 30Å catalysts.

New tests with different experiment conditions and different catalyst composition are underway. A more complete summary of the results for the binary

ferrihydrite catalysts have been prepared for publication [4].

### **Publications**

1. J. Zhao, F. E. Huggins, Z. Feng, F. Lu, N. Shah, and G. P. Huffman, *J. Catal.*, in press.
2. Z. Feng, J. Zhao, F. E. Huggins, and G. P. Huffman, *J. Catal.*, in press.
3. J. Zhao, Z. Feng, F. E. Huggins, N. Shah, and G. P. Huffman, ACS, Fuel Chem. Div. Preprint, V38, 196 (1993)
4. Zhao, J., Feng, Z., Huggins, F. E., and Huffman, G. P., submitted to *Energy & Fuels*.

Table 1. Coal liquefaction experiment conditions and products analysis.

Coal: Blind Canyon (Decs-17)

Coal loading: 5 g

Tetralin/Coal = 2 : 1

Catalyst loading: Fe/Coal = 0.6%

S(DMDS)/Fe = 2 : 1

Reaction temp: 380°C

H<sub>2</sub> Pressure: 800 psi

Reaction time: 60 min

Liquefaction products analysis

Sample	Oil	Asphaltene	Preasphaltene	Gas	Total
30Å	18.7	42.9	9.0	2.4	73.0
ferrihydrite (M/Fe<0.01)	22.7	38.1	12.4	2.2	75.4
Si <sub>0.05</sub> /ferrihydrite	23.8	40.6	7.6	2.3	74.3
Al <sub>0.5</sub> /ferrihydrite	24.7	37.0	8.0	2.2	71.9

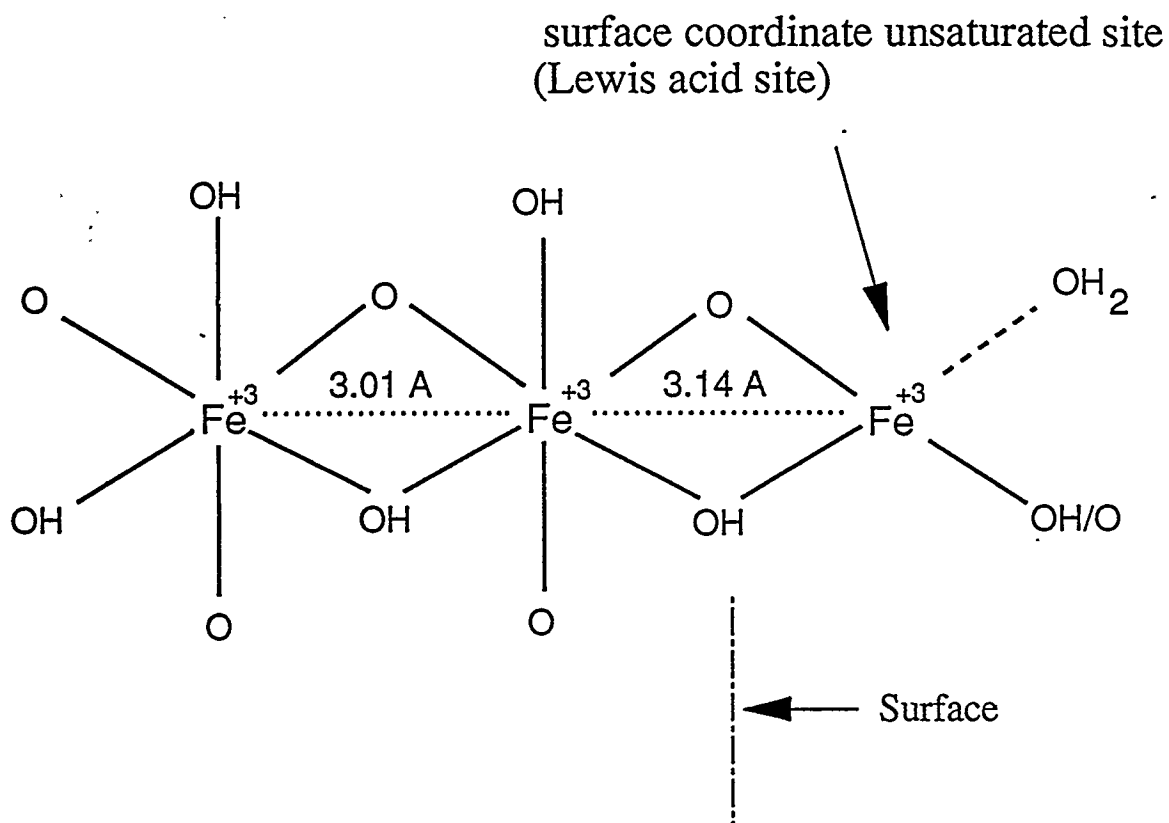


Figure 1. Proposed structural model for ferrihydrite (30Å catalyst).

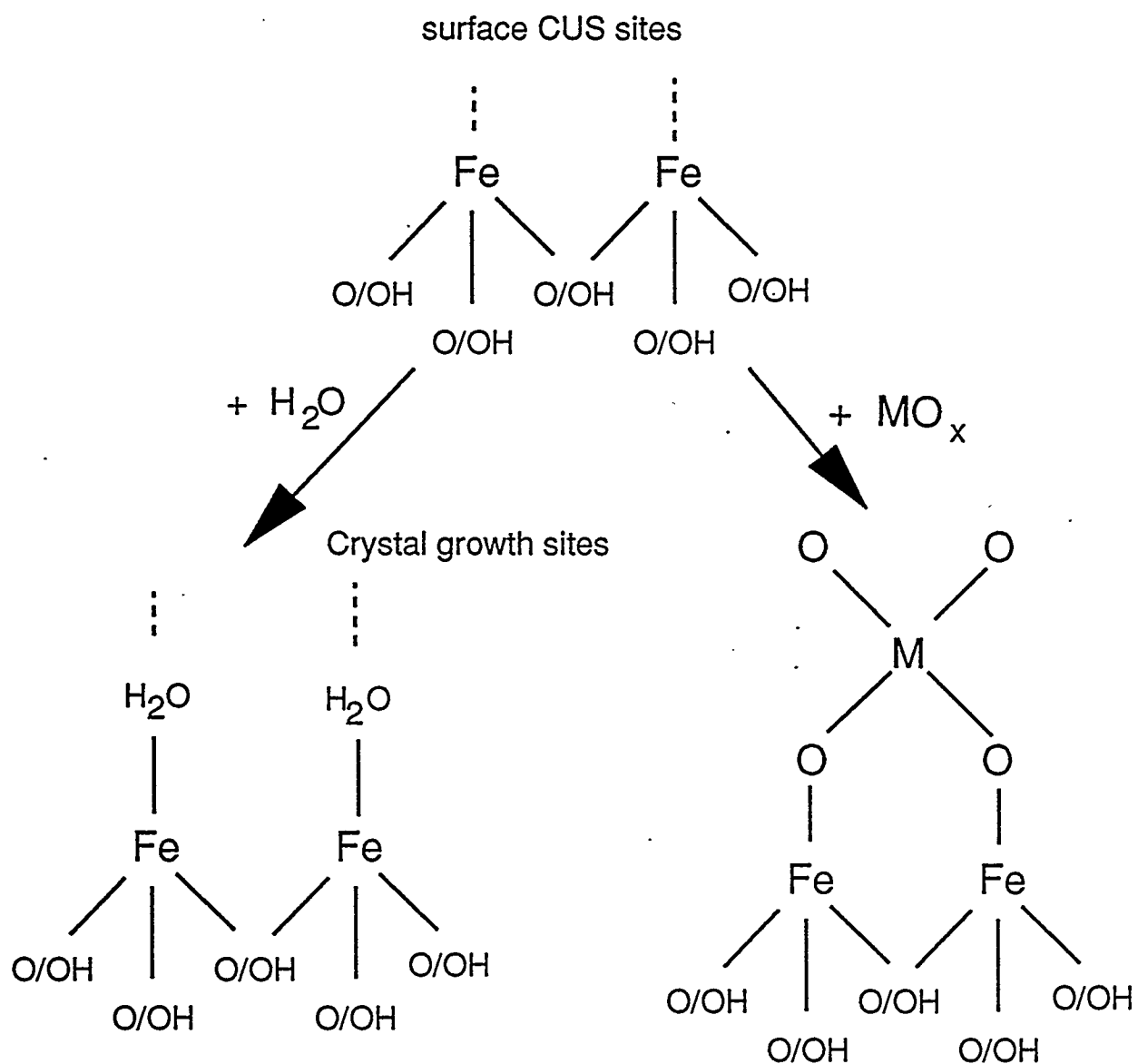


Figure 2. Chemisorption at ferrihydrite surface.



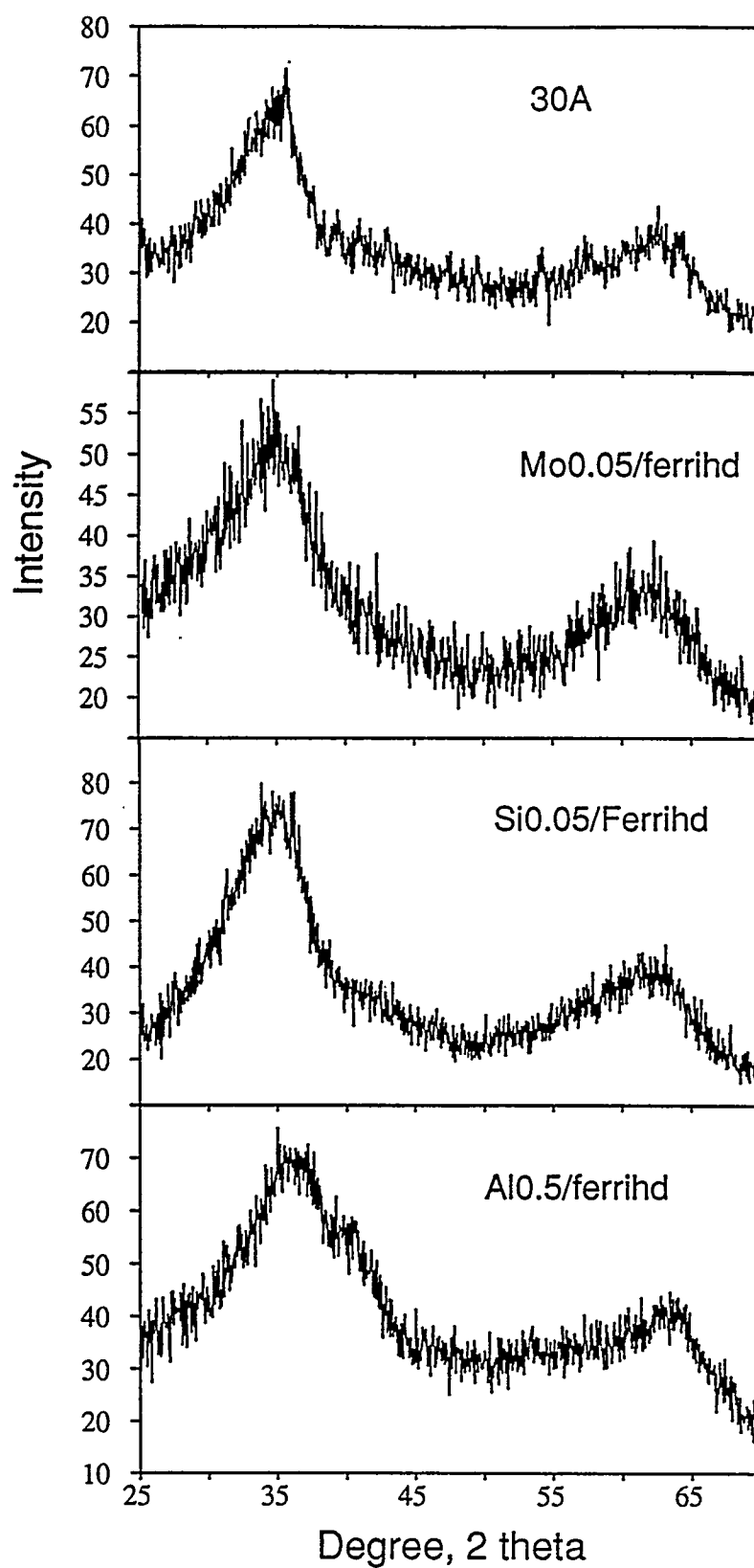


Figure 3. XRD of the 30A and the binary ferrihydrite catalysts.

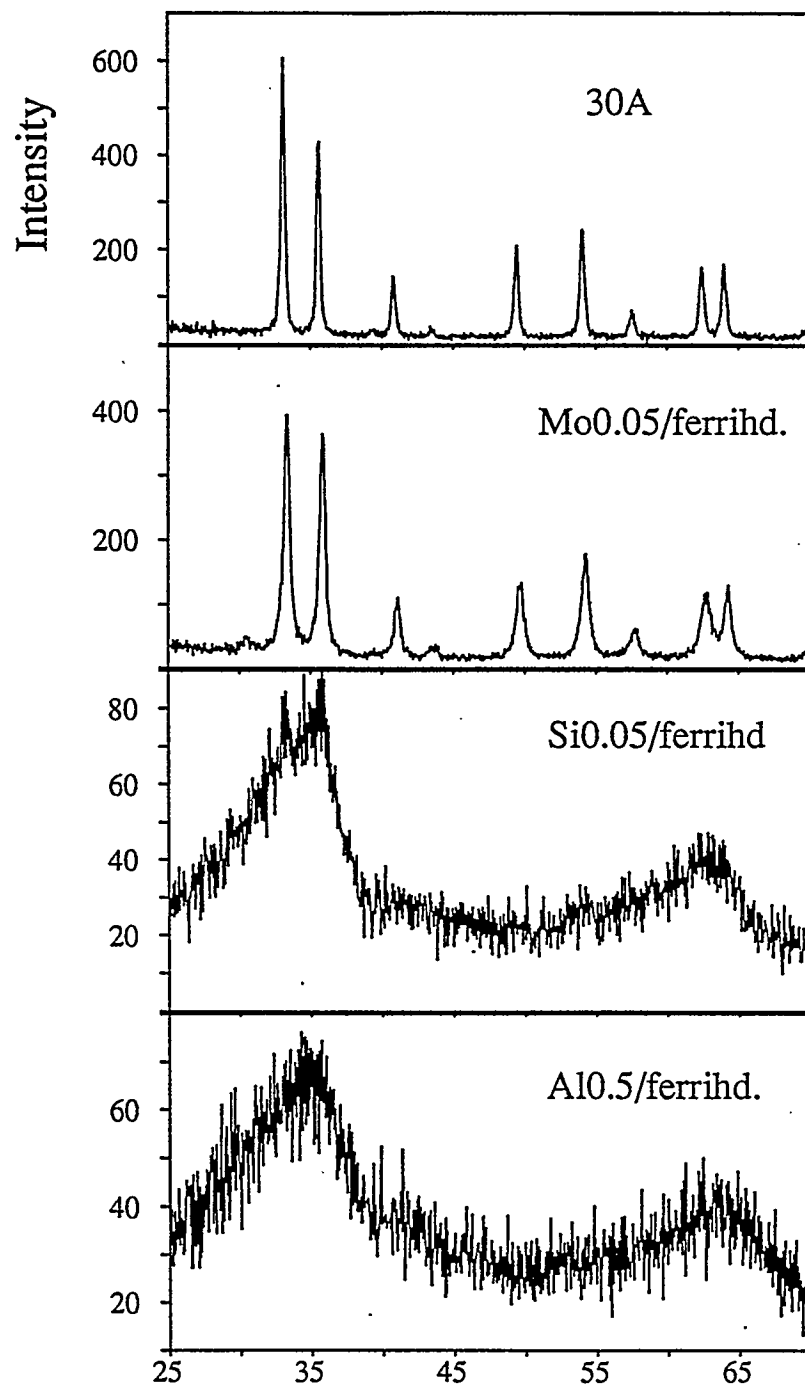


Figure 4. XRD of the binary catalysts after annealing.

### **I.3.4 COLIQUEFACTION OF COAL AND PLASTIC WASTES**

Due to an ever increasing volume of plastic products, sanitary landfills can no longer continue to be the major means for plastic wastes disposal. In the United States, disposal of plastics comprises as much as 40% of the volume of landfills. Plastics recycling appears to be a possible alternative solution and has the potential for high growth. However, the recycling of plastics that takes place currently is not due to industry initiatives, but because of government edicts. In the United States, laws are in effect in states such as California, Oregon, and Wisconsin that require plastic bottles to be made of at least 25 wt% of recycled plastic. Similar laws in other states and federal laws are likely to follow.

In 1990, about 0.4 million tons of plastics in the form of soft drink bottles entered the municipal waste stream, of which 31.5% was recovered. However, out of seven million tons of total plastic wastes in the same year, only 3.7% was recycled. Conventional plastic recycling always faces the problem of contaminated and mixed plastic scrap, which cause difficulties in the recycling. Conventional pyrolysis, as an alternative for plastic waste recycling, usually results in unsaturated and unstable oils of low yield and low value that can be used only for combustion.

Considering current conditions and expected future trends, of all the options that exist for plastics recycling, liquefaction should be considered seriously. Liquefaction of plastic wastes can not only provide a solution for plastic disposal, but can also generate an environmentally acceptable transportation fuel.

Scientists from Consortium for Fossil Fuel Liquefaction Science (CFFLS) have initiated a broad range of studies on the feasibility of coliquefaction of plastic and rubber wastes with coal. To expedite these efforts, a bibliography has been completed and distributed to all interested CFFLS scientists to serve as a source of theoretical and practical references for many topics of interest. The listed information is based upon available data as of the end of January 1993, primarily from chemical and engineering databases. It contains an extensive array of general and technical data, condensed from about one thousand articles, that represent the most important and relevant guidelines. The references are listed in alphabetical order by title in two

parts, plastics and rubber. A key word classification is also included for further subdivision of topics. In addition, the abstracts of articles that are considered to be most relevant are enclosed.

In our preliminary experiments, liquefaction studies carried out on polyethylene and polyethylene terephthalate waste by one stage tubing bomb reactor in fluidized sand bath using two different catalysts. At temperatures range from 400°C to 450°C, residence times from 15 to 60 min., and a hydrogen pressure of 800 psi cold the effects of both catalysts on the depolymerization of plastic materials and on the oil yields were examined. Comparative experiments were performed for coliquefaction of mixture of a medium density polyethylene (PE) and Blind Canyon coal. Saturated oil, consisting of mainly straight chain alkanes and alkenes and some light hydrocarbon gases, was produced from liquefaction of both polyethylene, polyethylene terephthalate and the coal-polyethylene mixture. The residence time at which the reactions were completed is estimated to be 45 minutes in this experimental conditions. The results obtained summarized in Table I. Oil yields of 88 percent were obtained from liquefaction of polyethylene and 93 percent from liquefaction of polyethylene terephthalate during these experiments.

Table I. Experimental results obtained from liquefaction of plastics, and coliquefaction of plastic/coal mixtures.

Sample	Additives	Temperature(C)	Total Conv.%	Oil Conv.%
PET	HZSM-5	420	100	92
PE	HZSM-5	420	100	88
PET	HZSM-5	400	100	90
Milk jug	HZSM-5	420	100	86
Coke Bottles	HZSM-5	420	100	93
lignite:PE 1:3	Fe-exch.+DMDS	450	91	83
lignite:PE 1:2	Fe-exch.+DMDS	450	67	51
lignite:PE 1:1	Fe-exch.+DMDS	450	53	40
PE	Tetralin	450	100	33
BC Coal:PE 1:1	Tetralin	450	70	42
BC Coal:PE 1:1	30Å FeOOH+DMDS	450	48	26
PE	30Å FeOOH+DMDS	420	100	76

PE = polyethylene, PET = Polyethylene Terephthalate, DMDS = Dimethyl Disulfide  
BC = Blind Canyon coal, Fe-exch. = Iron ion-exchanged Beulah lignite